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I. TH. ROSENQVIST

Subsoil Corrosion of Steel

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I. TH. ROSENQVIST

SUBSOIL CORROSION
OF
STEEL

1961

THE NORWEGIAN ACADEMY OF TECHNICAL SCIENCE, TRONDHEIM
NORWEGIAN GEOTECHNICAL INSTITUTE, OSLO

The increasing use of iron and steel in underground constructions such as pipelines, sheetpiling and foundation piles has rendered the problem of subsoil corrosion most urgent. The chief purpose of this publication is to give potential users of iron and steel the benefit of the modern viewpoints in this field.

Underground corrosion is treated as a complex of electrochemical processes which can be divided into anodic and cathodic reactions. The importance ot the cathodic reactions in determining the rate of corrosion is stressed especially.

The theory of the Norwegian Geotechnical Institute's corrosion probe is given, together with a description of the instrument and its use. This probe enables prediction of actual corrosion rates in different soils.

Methods of corrosion protection are described, with particular emphasis upon cathodic protection.

ERRATA

p. 6, 5th line from below, please read: after *three* years of exposure . . . . .

p. 9, 5th line from top of text column, please read: *than in soil* free from sulphide, ...

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PREFACE

The present publication dealing with subsoil corrosion of steel is the result of work carried out at the Norwegian Geotechnical Institute during the last eight years. In the bibliography, references are given to several papers dealing with underground corrosion. In all these cases the material consisted of metals buried in trenches in the topsoil. For engineers concerned with the foundation of buildings upon steel piles rammed to firm bottom, these experiences are of limited use. In many countries, and especially in Scandinavia and Canada, young marine deposits form the underground. Only the upper parts of these deposits have adjusted themselves chemically to the oxygen content of the atmosphere. The deeper parts may have very different compositions and aggressivities towards steel. Experiences from trenches in the topsoil may therefore be misleading. This is the main reason for the present publication.

The work is a result of co-operation with the staff at the Norwegian Geotechnical Institute, mainly with my old friend and colleague Johan *Moum* who has taken part in the investigations. I render him my most sincere thanks for his helpful co-operation.

Chapter 4, dealing with anaerobic bacteria and corrosion, is an edited version of two reports delivered by Emmy Egidius *Møllerud*, M. Sc. Whithout her aid this part of the publication could not have been written. I am very thankful for her help.

I thank also Mr. W. H. *Theakstone* and Mr. J. N. *Hutchinson*, who have read the manuscript and helped me in correcting the English.

Finally, I offer my thanks to the Board of Directors of the Norwegian Geotechnical Institute, for giving me facilities to write the manuscript and for having had sufficient patience to wait for the two years which have elapsed since I originally promised to have the manuscript ready for the printers.

Oslo, July 1960.

I. Th. Rosenqvist.

TABLE OF CONTENTS

Preface iii

Introduction v

Chapter I. Some fundamental points of view 1

Chapter II. Oxidation - reduction 15

Chapter III. Passivity - immunity - inhibition - overvoltage 19

- a. Passivity 19
- b. Immunity 21
- c. Inhibitors 23
- d. Overvoltage 24

Chapter IV. A survey of sulphate reducing bacteria and anaerobic corrosion by microbes of iron 27

- a. Sulphate-reducing bacteria, their occurrence, growth conditions etc. 27
- b. Occurrence of sulphate-reducing bacteria in Norway 29
- c. Anaerobic corrosion by microbes of iron in a neutral soil 29
- d. References on anaerobic bacteria and bacterial corrosion 33

Chapter V. Previous views in Norway and in other countries about corrosion 37

Chapter VI. Antiquities as criteria of corrosivity 43

Chapter VII. The cathodic reactions 47

Chapter VIII. The corrosion probe 57

The theory of the corrosion probe 60

Chapter IX. Corrosion experiments in the field 65

Case records 66

The Nurse's Home, Drammen, 66; A/S Thor Dahl, Sandefjord, 68; Experiences from Gothenburg, 74; Uglum Bridge, Gothenburg, 75; The piles of the Norwegian State Railways, 76; Hafslund near Sarpsborg, 76; Oslogate, Oslo, 76; Persgangen, Oslo, 76.

Chapter X. Cathodic and anodic protection 79

- a. Cathodic protection 79
- b. Protection by means of sacrificial anodes 84
- c. Anodes with impressed d. c. 86
- d. Permanent anodes 87
- e. Semi-permanent anodes 88
- f. Non-permanent anodes 88
- g. Anodic protection 88

References 89

INTRODUCTION

Problems connected with the corrosion of steel in soils are of the greatest importance in all construction techniques. Steel or cast iron in one way or another is used as an integral part of the modern construction industry as of all other industries. Steel or iron may be used as pipe lines and as parts of foundations, either as foundation piles or as sheet piling, or as reinforcement steel in concrete.

All types of deterioration of metals by chemical or electro-chemical processes are included in the term *corrosion.* A common type of corrosion is normal rusting. The well-known reddish-brown iron oxides or iron-hydroxide compounds termed rust are not formed by other corrosion processes. Even in such other cases, however, the deterioration process is termed corrosion. For instance, we may consider the solution of steel in acids. In such cases the iron ions will mostly remain in the liquid phase as dissolved positively-charged hydrated ferreous or ferric ions. In other cases steel may be attacked by certain bacteria. The corrosion product may then be precipitated as a black, insoluble iron sulphide.

For civil engineers, who are not supposed to be specialists in modern chemistry or electro-chemistry, the advance in corrosion research during the last decades is more or less terra incognita. In this publication we intend to present the subject for a public consisting chiefly of people who in their daily work are prescribing or using steel for pipe lines, foundation piles or in some other way. It is therefore necessary to touch upon, and in part to deal more thoroughly with, the mechanism of corrosion from a modern point of view. However, it is implicit that the many intricate theories cannot be dealt with down to their fundamental basis. The public for which this work is intended will hardly be interested in such discussions. It is therefore necessary and inevitable in some parts to popularize and partly vulgarize the matter. For specialists in corrosion research therefore, we have to apologize for inaccurate presentations and popularizations. Such inaccuracies to a great extent may be blamed upon the author himself, as not being a specialist on corrosion research in the proper sence of the word. Partly, however, the popularizations are intended to make the publication more easily digested by the intended reader.

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CHAPTER I

SOME FUNDAMENTAL POINTS OF VIEW

The different processes included in the term "corrosion" can be described physically as processes bringing the metal object plus the surrounding medium into a state characterized by a minimum of free energy. Excluding gold, all metals in contact with air and water represent states of energy higher than the minimum. When all the different components found in soils are added to pure water and air, most of the metal/soil systems resulting represent a state which is so much higher in energy than the stable state that corrosion reactions will occur. The velocity of the corrosion process, however, is dependent not only upon the difference in free energy between the initial and final states, but to a greater extent upon the energy barriers which have to be passed between the two states. The energy barrier is called the energy of activation. Schematically the corrosion process may be illustrated by Fig. 1.

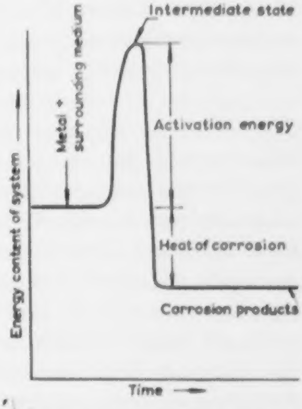

Fig. 1. Schematic picture of corrosion process of a minute element of a metal chrystal.

For several reasons it is not possible normally to calculate exactly the time necessary for complete deterioration of an object in a given medium. In most cases we have to depend upon empirical data. The corroding systems and the chemical composition of the media are in most cases so complex that our knowledge is insufficient for fundamental treatment. The metal silver, for instance, will be largely stable in non-saline soils, even after thousands of years. Prehistoric silver objects may be beautifully preserved in some cases. In other cases, as for instance in the Scandinavian marine clays, we have numerous examples of silver rings and brooches from the Viking Age which have been completely transformed into a soft mass of chlorides, so that not even traces of the metal are left. It is therefore a mistake to state that all "noble metals', are immune to normal corrosion.

For the civil engineer, however, what happens when silver is transformed into silver chloride, or when copper is tarnished by patina, is relatively unimportant. We are interested mainly in the process which attacks or may attack steel piles in different types of soil. Even in such cases corrosion can only take place if a difference in free energy exists between the initial and the final states, and provided all intermediate processes during corrosion are possible. The magnitude of activation energy must not be too high, as the soil temperature is normally low. In a given state there will always be an energy distribution between the different elements of the state, so that, statistically, at a given temperature some of the elements will possess an energy sufficiently high to pass over the activation energy hump. The logarithm of the number of elements which may pass this hump in the given time, $D = e^{-K/T}$, is proportional to the reciprocal value of the absolute temperature.

Corrosion processes attacking steel in soil are closely connected to electro-chemical phenomena. During corrosion an electric current passes from certain areas of the metal surface through the electrolytic conducting soil and back to other parts of the metal surfaces. It is seen that an attack on the metal takes place where the current leaves the metal surface and passes into the soil phase; this is where we have the positive terminal. In the place where the current enters into the metal there is no attack. In many cases the parts which at one time represent the positive terminal and the areas which represent the negative terminal may change whilst the corrosion process takes place. In such cases we get the impression of fairly uniform attack. At any given time, however, the areas where the electric current is leaving the metal and passing into the surrounding electrolytic medium are critical points in a long series of processes which altogether are necessary to cause corrosion. The presence of an electrolyte is the first condition for a corrosion process of this type. *Only soils which are electrolytic conductors are corrosive.* However, in practice this will mean that all soils are corrosive, as all natural soil contains smaller or larger amounts of a liquid phase, and this liquid phase as a rule will contain more or less amounts of different dissolved salts. It is not even necessary that the liquid phase contains alien ions, as chemically pure water has a certain electrolytic conductivity because of the dissociation $H_2O \rightarrow H^+ + OH^-$. In practice, however, the low degree of dissociation found in pure water free from any dissolved air or other contamination is not regarded as corrosive towards normal steel at normal temperatures. At higher temperatures, however, even pure water may attack steel. Other metals, as for instance the alkali metals, are attacked vigourously by pure water at room temperature. In the case of steel, it is necessary that the amount of soluble salts, acids or bases is raised above a certain limit for the electrolyte conductivity of the liquid phase to reach a sufficiently high value to involve noticable attacks by corrosion. Independent of the composition of the liquid phase, the fundamental processes are in principle equal for all types of electrochemical corrosion. In text books the corrosion processes frequently are illustrated by a dry cell battery. In this case we have two electrodes, namely the zinc anode which forms the container of the element, and the graphite rod in the center which forms the cathode. At the anode the current, and consequently also the zinc atoms, pass into the electrolyte between the graphite rod and the container. At the cathode the current enters the metal again passing through the electric bulb, and back to the zinc container. The electrodes in a pocket lamp battery consist of a metal and a graphite rod. However, in an electric cell they may consist of two different metals or even of two areas in the same piece of metal.

Under all circumstances a difference in electric potential is necessary to permit the electric current to continue. For steel foundation piles in soil, the anodes and the cathodic parts are formed mainly by different areas of the same pile. Under certain circumstances (for instance when the piles are driven through rubbish fills where they may come into contact with noble metals or copper) anodes and cathodes may consist of different metals. In other cases two different piles may be connected through the reinforcement steel of the building. In such cases one pile may be mainly anodic, whereas another pile may form the cathode. In any case it is necessary that the two different metals of the different parts of the same metal object are connected through a metallic conductor in order to form the necessary anodes and cathodes by the corrosion process. In this way we obtain a closed current circuit from the one metal through the electrolyte, which is formed by the soil, to the other metal, and then by metallic conduction back to the first metal.

There is a difference in principle between the conduction found in metals and the conduction through electrolytes. In metals the current transport takes place by negatively charged electrons passing from the most negative part to the most positive part of the conductor. The electrons pass almost without any obstacles in metals at normal temperature, and the temperature dependence is positive. This means that a rise in temperature involves a rise in the resistance to the flow of electrons. In the eletrolyte phase the electric current takes the form of movement of positively charged ions from the positive to the negative terminal, and of negatively charged ions passing in the opposite direction. The temperature dependence is negative, that is, a rise in the temperature of the electrolyte causes the resistance to the movement of the ions to diminish. The electronic conduction in metals occurs in proportion to the potential difference between the positive and the negative terminals. Any potential difference, even if very low, will give rise to a current. In electrolytic solutions, however, the conditions are different. A pronounced rise in conductivity is observed when the potential difference between the two electrodes reaches a certain limit, called the reversible potential. In addition we need a certain voltage for all finite current densities. The sum of the overvoltage and the reversible potential is called the dissociation voltage. The magnitude of the overvoltage depends upon the properties of the electrode materials, the nature of the electrolyte and the current density.

From a study of corrosion processes we find that the liberation of metal atoms takes place at the positive terminal, which we call the anode. Here different processes take place simultaneously: Positively charged metal ions leave the solid surface and enter into the solution; at the same time a corresponding number of negatively charged ions in the state of electrons are left in the metal. The positive ions move towards the cathodic areas, whereas the electrons distribute themselves in the metal object. Normally this metal object has adsorbed a layer of the liquid phase upon its surface. In this adsorbed layer of liquid the distribution of electrolyte ordinarily will be quite different from the distribution of the ions in the "free liquid phase". At the cathodic areas of the metal, the electrons in the metal will react with components of the electrolyte present in the diffuse border layer. Thus the electrons liberated at the anodes will be consumed, and the potential of the metal will rise. The cathodic process involves different types of reduction. They will only take place in the presence of substances which act as oxidizers under the given conditions. These oxidizing substances, however, may be of greatly variable nature. *It is imperative that both anodic and cathodic processes are possible in order to have corrosion.* It is not sufficient that one group of processes may take place, if the other series is impossible at any part of the metallic conductor.

In principle there is no difference between the process taking place when steel is dissolved in an acid and the process which takes place when a steel corrodes in soil. This latter is independent of whether the soil is acid or alkaline. For solution in acid the iron atoms of the anodic parts of the steel change into bivalent positively-charged iron ions, whereas the corresponding electrons move to the cathodic areas and combine with the positively-charged hydrogen ions of the acid, neutralizing them to neutral H-atoms. In the film of neutral hydrogen the atoms form pairs and leave as H_2 bubbles. Attack will take place only at the anodes, and the hydrogen bubbles are formed only at the cathodes, even though it seems as if the corrosion takes place all over the metal surface and not at well-defined anodes. This is due to a change between the anodic and cathodic areas with time. When iron corrodes in soil, the neutral iron atoms are transformed into bivalent positively charged iron ions in the same way, and the electrons are consumed at the cathodic areas. In soils, however, many different reactions may take place at the cathodes, not only the simple neutralizing of the positively-charged hydrogen ions. Normally we will have other active oxidizing components than hydrogen ions. For instance, we may have oxygen in water according to the equation

$$4e^- + 2H_2 + O_2 \rightarrow 4OH^-$$

In a similar way trivalent iron or tetravalent manganese may consume electrons, for instance according to the equation

$$e^- + Fe^{+++} \rightarrow Fe^{++}$$

This equation clearly demonstrates the reduction by the electrons. Even biological processes involve reductions. For instance anaerobic bacteria in their metabolism may use electrons from cathodic parts of the corroding steel as reductors. These bacteria live without the presence of free oxygen. Their necessary energy arises from the reaction between sulphate ions in the pore water and electrons, for instance according to the following equation:

$$8e^- + SO_4^{--} + 4H_2O \rightarrow S^{--} + 8OH^-$$

The sulphide ion subsequently may be oxidized to elementary sulphur. The action of these bacteria will be treated in a separate chapter.

In addition to this process we have the discharge of hydrogen ions to neutral hydrogen. This discharge is slowed down by the low concentration of hydrogen ions present in normal soil moisture, and by the low currents involved in normal corrosion process, as the ions first have to be neutralized, forming atomic hydrogen, which later couples to the hydrogen molecules. This hydrogen forms a layer upon the cathode. Investigations carried out at the Norwegian Geotechnical Institute, however, seem to point to a greater importance of hydrogen in this red-ox process than assumed earlier. (See later chapter.)

Together with other factors counteracting the consumption of electrons, the influence of the hydrogen film is included in the term "cathodic polarization". At the anodic parts the high concentration of iron ions tends to counteract solution. The influence of the concentration of iron ions is elucidated by the equation given by NERNST in 1889.[1] The equation named after him gives the potential difference between the metal and the solution as a function of the concentration of the respective ions in the solution. The electric reaction may be expressed in the following manner:

---

[1] See references at the end of the paper. The capitalization of the author's name has been made the first time a work is cited.

$$M \rightarrow M^{n+} + ne^{-}$$

The electric potential E is given by the following equation:

$$E = \text{const.} + (RT/nF)\ \ln C_{ion}$$

Here R is the universal gas constant, T the absolute temperature, F = Faraday, n = the number af electrons which take part in the reaction, and $\ln C$ is the natural logarithm of the concentration of metal ions in the solution. (For accurate treatment we have to use the activity of the ions instead of the concentration of the ions. In dilute systems, however, these figures will be very close to each other.) For processes which take place with a finite velocity, we can understand that the concentration of ions at the surface depends upon the diffusibility of ions in the adsorbed film. If we apply the normal values for R and F in the above equation and transform from a natural logarithm to Brigg's logarithm, we obtain the result that a variation in the concentration of iron ions by a power of ten corresponds to a change in potential of about 28 mV at normal soil temperatures. This is because two electrons take part in the reaction of one iron atom. This change in potential tends to counteract the solubility of the iron and form an integral part in what is called the anodic polarization. The cathodic and the anodic polarization will both tend to slow down the velocity of corrosion. If it were not for such factors, no steel object could persist in a normal soil regardless of the composition of the pore water. The anodic, and especially the cathodic, polarization phenomena depend upon the nature of the material, the nature of the surrounding medium and the corrosion current. The influence of all these phenomena tends to approach the anodic and cathodic potentials. Thus the driving force is diminished by the corrosion process. For steel in soil the cathodic potential closely approaches the anodic potential, as seen from Fig. 2 (LaQue, May, and Uhlig, 1955). Normally we find that the anodic polarization is less important than the cathodic polarization in the slowing down of the corrosion process. (The different electron reactions at the cathode are included in the term "cathodic depolarization"). Consequently, these processes will be important as controlling factors for the continuation of the corrosion.

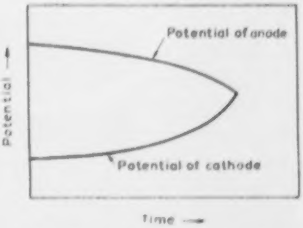

Fig. 2. Shift in potential of cathode and anode by increasing polarization with time.

As seen above the corrosion processes are treated without even mentioning the word "rust". However, it is common mentally to connect the formation of rust with the corrosion of steel and iron. The reason why rust is not mentioned is that the precipitation of rust is a *secondary process,* which does not necessarily have to take place, as for instance in the solution of steel in acids. The same holds in neutral media, provided the addition of oxidizing materials is kept sufficiently low. In such cases we will have the formation not of rust, but, for instance, of a black reaction product called hydromagnetite, which has the formula $Fe_3O_4 \cdot nH_2O$; this is different from that of rust, $Fe_2O_3 + FeO(OH)$. The precipitation of rust will only take place when hydroxile ions, together with oxygen in sufficient amounts, react with bivalent positively-charged iron ions formed by the anodic process. The first reaction which takes place is that the bivalent iron ions react with the hydroxile ions, forming ferrous hydroxide, which in the next step is oxidized by the oxygen of the solution, forming ferrous hydroxide and oxide, i.e. rust. Dependent upon the intensity of the corrosion current, the content of oxygen in the liquid phase and the degrees of movement in the liquid, the rust may form either directly on the corroding surface or at some distance from it. For steel foundation piles in soil it seems as if the formation of rust is quite insignificant, or does not take place at all. The same may be seen when reinforcement steel in concrete corrodes under special conditions. In this case, however, we will frequently find the formation of rust, but at some distance from the steel.

As an illustration of the corrosion process we will indicate a laboratory experiment, (se Fig. 3). The desiccator is full of sand. A glass pipe connected to a rubber tube leads from the bottom of the desiccator to the bottom of a bottle placed beside it. The bottle, the desiccator, and the tubes are filled wih a mixture of sea water and tap water. Some 7″ steel nails have been placed in the sand so that the heads of the nails are just above the sand surface. This is intended to be a model of a foundation. The nails in the wet sand undergo continuous corrosion, sending positively-charged iron ions into the solution. The corresponding electrons are consumed in the upper part of the nails because of reduction-oxidation processes, as the oxygen from the atmosphere enters freely into the upper part. Because of evaporation from the sand surface the water level in the desiccator sinks, causing suction which brings water over from the communicating bottle into the desiccator. When the water level has sunk about 1 cm, additional water is placed in the desiccator, so that the old water level is re-established in it and in the bottle. This involves transport of water from the deepest part of the desiccator into the bottle. This water brings with it some of the dissolved iron ions. In the bottle these ions are slowly oxidized from the bivalent into a trivalent state, and precipitate as rust. When the picture was taken after half a year of experiment, the amount of rust in the bottle was quite considerable. Thus we can see that the formation of rust may occur far from the place where the iron corrodes. Therefore it cannot be guaranteed that the iron objects do not corrode simply because no rust is found on them. In Fig. 4 we can see what the nails looked like after one and a half year of exposure. The nails have corroded mainly in their lowest parts, whereas the upper part is quite undamaged. Thus we get the impression that it is water of low oxygen content in the deepest part of the desiccator which is corrosive, whereas the upper water with high oxygen content should be harmless. The circumstances, however, are that the oxidizing process which takes place on the upper part of

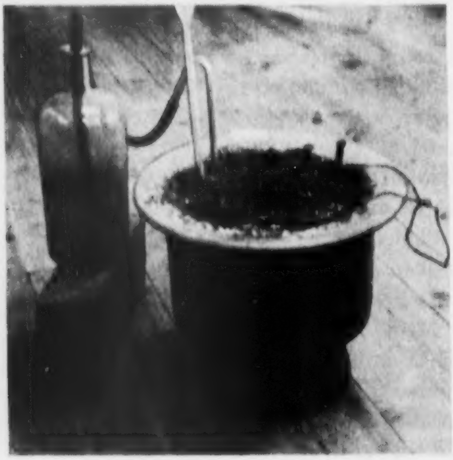

Fig. 3. Laboratory experiments showing the formation of rust in the bottle to the left whereas the corroding iron is situated in the dessicator to the right.

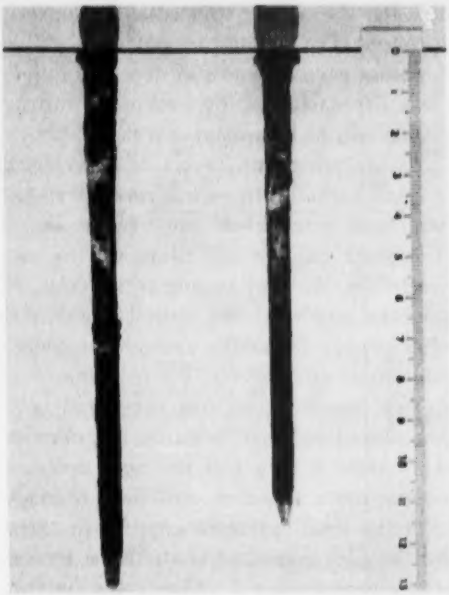

Fig. 4. The nail to the right is severely corroded at the point after $3^{1}/_{2}$ years' exposure in the dessicator Fig. 3. The nail to the left is also corroded at the point after $2^{1}/_{2}$ year of exposure.

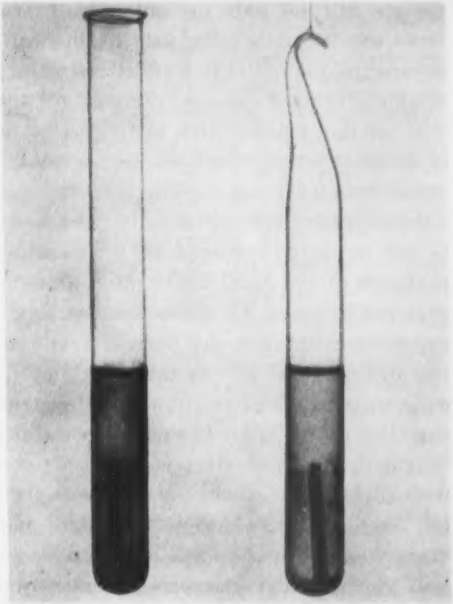

Fig. 5. Two steel rods in 3.5 % NaCl solution. To the left under aerated conditions, to the right no air permitted.

the nails has caused the corrosion in the deepest parts where the water is poor in oxygen. If it had not been for the presence of oxidizing agents at one place in the system, the corrosion would have been minimal. This is the case in many places where we have examined steel piles drawn up from the ground, and it is seen if we place steel in salt water free from oxygen. In Fig. 5 the action of oxygen is illustrated. In both reagence tubes, a piece of soft iron rod is placed in a 3.5 % solution of sodium chloride. The one reagence tube was melted off at once, whereas the other was left open, and the evaporating water was replaced by distilled water. After one and a half years the experiment was stopped, and the steel wire rods examined. We found that the wire in the open tube then had decreased 0.304 mm in diameter, whereas the wire left in the tube which was melted off had only decreased 0.004 mm in diameter. In both cases the conductivity of the water was the same, but the amount of reducable materials (oxygen) had been higher in the open tube than in the closed one. The piece of steel which had been in the closed reagence tube had been highly polarized cathodically, whereas in the open tube depolarization due to oxygen had been permitted. If more active depolarizators, as for instance hydrogen peroxide or tetravalent manganese, or strong acids had been added, the corrosion would have been still more rapid. This points to the importance of the cathodic depolarization.

The cathodic depolarization reactions do not take place with the same velocity at all metal surfaces. In other words, some metals are more easily polarized than others. It is therefore necessary to have a knowledge of the polarization and depolarization conditions and not only the potential difference between the anodic and cathodic parts if we want to predict the rate of the corrosion process. The change in potential called polarization is not only a function of the total corrosion current, but also depends mainly upon the current density. We may for instance take depolarization by hydrogen, and we will see that this reaction between electrons and ions will be spread over a large surface if we have a large cathode and a small anode area, forming thin layers of neutralized atoms which are more easily removed than for a small cathode. In such a case we would have a greater current density. The hydrogen will form a relatively thick layer, and it is not so easily removed by a secondary reaction with oxygen. To illustrate the importance of the areal distribution between the electrodes, we may couple two metals, so that the one will form the cathode and the other the anode. If for instance steel and copper are coupled, the normal event will be that copper forms the cathode and steel the anode, if this pair of metals is placed in a solution of electrolytes. We may take two congruent pieces of steel and combine them with two copper plates, one very small and the other very large. If these two metal pairs are placed in a salt solution, we observe that both pieces of steel will corrode more quickly than if they had not been coupled with copper. The steel combined with the large copper plate, however, will corrode much more quickly than the piece of steel coupled with the small plate of copper. In these cases the increased velocity of corrosion is due to the fact that electrons set free by the iron atoms changing into iron ions are more easily consumed on a copper cathode than on an iron surface. However, even in cases where the cathodic area was steel, we would have observed a corresponding relation between large and small cathodes. With the nails in the desiccator containing sand, the depolarization took place on the upper part of the nails. If we had used a nail with a large plate on top, and placed it under pure oxygen instead of air, corrosion at the point of the nail would have occured much more quickly. In engineering construction this means that steel foundation piles driven through ground of variable composition will involve the greatest possibility of failure if the ground consists of thick layers where the depolarization is high and thin layers of low polarizability. In cases of thin layers with high oxidizing power and thick layers of low polarizability, the danger of failure is much less. On the other hand, if we have a homogeneous profile of low oxidizing capacity, the soil will be less dangerous than a homogeneous soil of high oxidizing capacity along the whole extent of the pile. In construction, however, it is important that no part of the pile or the beam should fail. Therefore the danger of serious failure increases with the length of the pile, as the possibility for large cathodic and small anodic areas will inevitably increase for all material that is not a 100 % homogeneous medium (Figs. 6, 7).

A further factor causing corrosion is the variation of salinity through the soil profile. The Nernst equation mentioned above shows the electric potential as a function of the activity of the ions liberated by corrosion in the surrounding medium. When the equation was given it was mentioned that the activity was proportional to the concentration of the ions. However, this is only the case if the amount and nature of other salts are constant. If the salt concentration changes, the activity of a given ion will change simultaneously, even if the concentration is kept constant. Normally the result will be that in areas where the concentration of alien salts is high, anodes will develop, and cathodes will develop where the concentration of salts is low (Fig. 8). In this connection we must mention also the effect of sulphides in the soils. Most Scandinavian clays contain small amounts of sulphide due to bacterial activity. As the solubility of ferrous sulphide is markedly

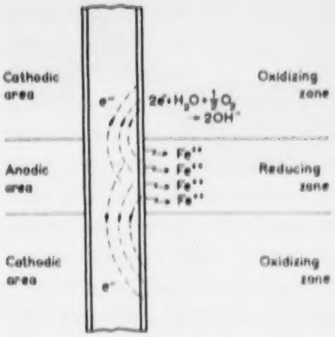
Cathodic area
Oxidizing zone
e^-
$2e^- + H_2O + \frac{1}{2}O_2 = 2OH^-$
Anodic area
Fe^{++}
Reducing zone
Cathodic area
Oxidizing zone
e^-

Fig. 6. Localization of corrosion due to humus-bearing layer in oxidized soil.

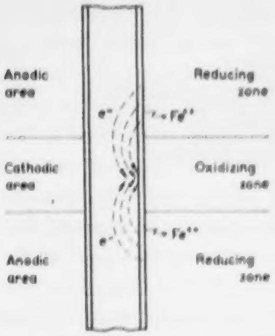
Anodic area
Reducing zone
e^-
Fe^{++}
Cathodic area
Oxidizing zone
e^-
Fe^{++}
Anodic area
Reducing zone

Fig. 7. Localized corrosion due to oxygen-bearing gravel seam in reducing soils.

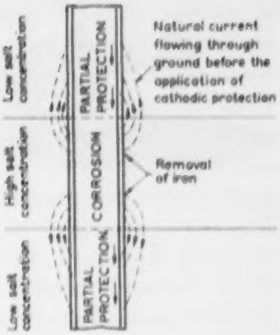
Low salt concentration
PARTIAL PROTECTION
Natural current flowing through ground before the application of cathodic protection
High salt concentration
CORROSION
Removal of iron
Low salt concentration
PARTIAL PROTECTION

Fig. 8. Localized corrosion due to variations in salinity.

lower than the solubility of ferrous hydroxiles, the concentration of iron ions around the anodes in sulphide-bearing media will be much lower than the concentration around anodes in media free from sulphide at the *p*H values normally found in the ground. This means that the anodic polarization will be markedly lower in sulphide-bearing soils free from sulphide, and even though the anodic polarization is of relatively less importance than the cathodic polarization, it is not to be neglected. Another factor is that where high sulphide concentrations are found, we will normally have spontaneous formation of anodes, whereas cathodes will form where the sulphide concentration is low or absent.

The corrosion process of steel piles in soil is normally so slow that really noticeable effects need months or years to develop. It is therefore not normal to follow corrosion processes by visual examinations alone. As stated above all the processes dealt with will be of an electric nature: Therefore it seems possible that by means of suitable electric measuring devices, most of the factors causing corrosion might be investigated. One type of such a measuring device which registers factors causing corrosion has been developed by the Norwegian Geotechnical Institute. This corrosion probe is dealt with in a later chapter. When such instruments are used, we need to know the model laws. This is a very intricate question, however. The physical and chemical basis is not sufficiently well known, and we therefore have to depend upon empirical relations. However, the empirical parameters suitable for the marine clays in the Oslo region probably are not fully valid in other soils. For instance in France and in the Tropics the interpretations of the instrument readings most probably will be different from those arrived at in Norway.

By means of chemical colour reactions we may show some of the general principles in corrosion. Normally such tests are carried out with models, using jelly instead of clays as a corrosive medium. For instance, if an alginate jelly containing potassium cyano-ferrate (III) and phenolphthalein is prepared, we have a model substance which is transparent, and which will react to the presence of ferrous ions and hydroxile ions. Bivalent iron ions will cause a red colour with phenolphthalein. To such a jelly we may add various electrolytes in order to have a composition similar to the pore water in various clays. We may adjust the conductivity, the *p*H and the depolarizing capacity within wide limits. If an ordinary nail is placed in such a jelly, we will observe that the blue colour develops at the point and head of the nail, whereas a red zone is formed along the middle part of the nail. From this we infer that the parts of the steel which have been mechanically treated in the cold state will easily form anodes where the corrosion takes place. The central parts of the nail which have not been mechanically deformed will then be cathodic towards the deformed parts of the nail. This is due to the internal stress energy hammered into the steel wire during the manufacturing of the nail. The iron atoms in this part of the nail have a higher escaping tendency. The mechanical influence exerted upon the steel during manufacture is consumed by the following process:– One part is necessary to overcome the internal friction in the steel; this part is directly transformed into heat; another part is necessary for the plastic flow of material: even this part is transformed into heat, but a smaller part is left as stress energy in the steel: this energy is relieved again when the steel corrodes. As an example we may think of a watch spring which is wound up. This spring will contain a certain mechanical energy. If the spring is dissolved, for instance in hydrochlorid acid, the heat developed will be higher than that developed for a spring which is not wound up. If two such springs in different states of stress had been coupled through an electric conductor and placed in a homogeneous electrolyte, the spring which was highest in energy would have been the anode, whereas the other would have been the cathode. Consequently the wound spring would have behaved as a less noble metal than the unwound spring.

In many cases worn-down railway or train rails are used as foundation piles. In such cases we may observe an actual example of the importance of stress conditions. At the laboratory of the Norwegian Geotechnical Institute we have found potential differences as large as 30 mV between the head and the rest of the same rail when pieces of a steel are coupled through a voltmeter of high internal resistance and placed in a 3 % solution of sodium chloride. If we take the same measurement using material from a new rail, we may find a small potential difference also, but in such a case the difference will normally be the other way round, so that the head of the rail behaves as the most noble metal. Therefore if worn-down rails are used as foundation piles, we will find normally that the head of the rail forms the anodic part, whereas thinner parts of the rail will be protected against corrosion as they form the cathodic parts. Most probably this will be an advantage mechanically, as the corrosion in the thin parts of the rails will decrease the stiffness of the piles which prevents buckling. The total loss of iron due to corrosion of a used rail probably will be somewhat higher than in cases where the steel has been annealed before driving.

Another type of mechanical stress may be introduced in the steel pile material during welding. In laboratory experiments as well as in extracted test piles we have seen that the corrosion has been intensified at a distance of about 1 cm from the weld seam. This is obviously a harmful factor, and we have reason to believe that overheated welds may cause serious danger of corrosion.

For most pile foundations we must expect that the piles are not driven completely vertically, but are somewhat buckled. When such piles are loaded, we will have tension and compression stresses in different parts of the material. This uneven distribution of stresses will cause differences in potential, and may cause local corrosion.

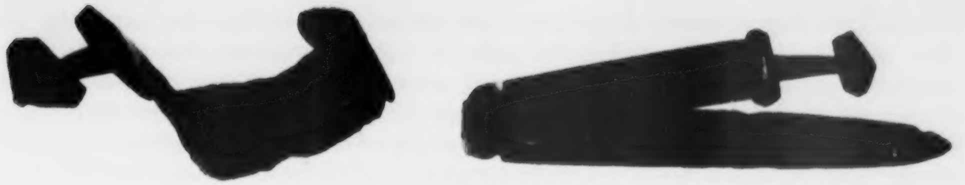

Fig. 9: Localized corrosion due to stresses in a bent Viking Sword. The corrosion in the bend (to the left) protected the rest of the sword from attack.

We must be aware of the special type of corrosion which is called *stress corrosion.* It is well known that in metal objects which have been exposed to very great mechanical stresses close to the yield point a specific type of attack may develop between the single metal grains, and also across such grains. We have intra- and inter-metallic corrosion. The attack leads to cracking of the metal in the parts which have been exposed to tensional stresses. It looks as if the metal is broken mechanically as a consequence of the stress. In reality, however, we have to consider electrochemical corrosion. Although such corrosion phenomena are well known from laboratory tests and from other practice, we do not as yet know any example of such corrosion of steel piles in ground. This, however, may be due to the very limited material we have been able to examine, as none of the test piles extracted have been very highly loaded. Such tension and compression stresses of course will develop only on piles carrying loads, and not on unloaded test piles.

Beautiful examples of the importance of stress corrosion may sometimes be seen in archaeological objects. From Roman time to the Viking Age it was fairly common in Scandinavia to bury the dead along with their arms and other equipment. At some funerals and in some votive deposits the arms were destroyed (killed) before deposition. The swords were bent, the axes were beaten to pieces, and the shields splintered. In cases where such depositions of arms were placed in soils of very low corrosive power, we may observe that the corrosion has been localized at those parts of the bent swords which have been under stress, i.e. the apex of the bend. In some cases this corrosion has been the only attack, or the chief part of the corrosion has taken place at the parts of the sword where the maximum mechanical stress occured. Probably these specific localized corrosion phenomena are restricted to steel of a certain carbon content, i.e. steel having a certain hardness, whereas the typical wrought iron swords could not arrive at a sufficiently high state of internal energy, even when the swords were bent. In the same way swords which have been heated after the bending, for instance in cremation, will not show localized corrosion, as all stresses have dissappeared on the funeral pyre which acted as an annealing agent. Fig. 9 demonstrates this localized corrosion on a sword from the early Viking Age.

These examples point to the importance of mechanical working and of compression and tension stresses on the corrosion potential of steel. It is the same as the case of the worn-down rails used as foundation piles. In the case of the sword we have to infer that if the sword had not been bent, the total corrosion would have corresponded to about the same amount of iron, but the loss would have been distributed evenly. In the case of the pile it is unimportant whether the pile fails because of the localized corrosion or because the whole pile had been corroded.

All corrosion processes depend upon the temperature, in much the same way as does any other chemical reaction. Not only the temperature itself, but also the temperature gradients are of importance, and may cause non-localized attacks. Investigations carried out by J. Moum and the present author (1957) have given us some knowledge of the temperature variations in Eastern Norway. The annual variations decreased rapidly with depth, and below 6–7 m the temperature differences are less than one tenth of a degree centigrade. Above these depths steep gradients may occur in summer and winter. This knowledge of the temperature variations, however, is most important in case of unheated foundations, i.e. foundations of bridges, monuments etc., whereas most piles used for foundations of houses will be exposed to other temperature conditions due to the heating in the buildings. There is therefore no general rule as to the temperature gradients in the ground. The principle, however, may be discussed. If a steel rod is exposed to a chemically homogenous medium having steep temperature gradients, the parts of the rod which are at the highest temperature will form mainly the anodes, whereas the colder parts will form the cathodes. For natural variations under non-heated foundations therefore we have to assume a tendency towards a shift between the cathodic and the anodic parts during the year. For piles under houses we do not get the winter cooling, and the upper part of the pile will have a tendency to be permanently anodic. The temperature gradients, however, are of less importance than the chemical gradients, and it may very well be that the upper parts will form cathodes although they are warmer than the bottom part.

As mentioned, the temperature in itself is of importance for evaluating the rate of corrosion. The inorganic corrosion processes increase their velocity with increasing temperature. As a rule we may say that most chemical reactions double their velocity for a temperature increase of 10° centigrade. However, this may be variable, depending upon the magnitude of the activation energy. For corrosion processes an increase of 6–8° may in many cases be sufficient to double the rate of the attack. For the biological, i.e. the bacterial attacks, the conditions are more complex. The metabolism of the bacteria is slowed down to insignificant values by a lower temperature. It increases rapidly within a narrow temperature interval, and at the highest temperature, when the bacteria are unable to live, the process stops entirely. Therefore, the attack caused by bacteria under heated foundations may be very much different from that under unheated foundations of bridges etc.

We may sum up the preceding points and conclude that the corrosion of steel in soil is a function of the following factors:

1. The quality, composition and mechanical stress situation of the steel.
2. The depolarizing properties of the soil.
3. The electric conductivity of the soil.
4. Variation in the degree of depolarizability at different parts of the pile.
5. Variation in salt against different parts of the pile.
6. The temperature of the surrounding soil.
7. Variations in temperature.
8. Percolation of water through the soil.

The last mentioned factor is of special importance for anodic polarization.

With our present knowledge of the mechanism of corrosion we hav to introduce empirical values based on experience for each of the factors listed. We need a very complex experiment programme in order to ascertain the value of each of the factors. In all observations until now so many variables have ben involved that we may be in doubt as to which of several factors has been of the greatest importance.

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CHAPTER II

OXIDATION - REDUCTION

Oxidation and reduction are names for the same process. If a substance is oxidized, some other compound has to be reduced simultaneously. The typical oxidation-reduction process is represented for instance by the reversible equation $Zn + Cu^{++} \rightleftarrows Zn^{++} + Cu$. Under normal conditions this reaction will go from the left to the right. The result is an oxidation of metallic zinc to zinc ions, and reduction of the copper ions to metallic copper. If, however, the concentration of copper ions is sufficiently low, the reaction according to the Nernst equation will go the other way. If we consider the electromotive force for a cell $Zn/Zn^{++}//Cu^{++}/Cu$, we understand that this electromotive force depends upon the activity of all the four components of the cell. Therefore it is not possible to speak about the oxidating power of the substance. We may only compare the oxidizing power for each special group of substances with the reducing power of another group. In the example mentioned we are comparing the group Zn/Zn^{++} with the group Cu/Cu^{++}. If we want to express numerically the reducing or oxidizing power of different groups, we have to choose a reference group which may be given no reducing and no oxidizing power. Conventionally we have chosen the standard hydrogen electrode as the point 0 in our scale. Such an electrode is represented by one atm. hydrogen in contact with one-normal solution of hydrogen i.e. one-normal acid. Such a cell consists normally of a platinated piece of platinum. Because of the platination this platinum has obtained a large specific surface. This electrode is placed in one-normal solution of an acid, and hydrogen gas from a hydrogen bottle is bubbled through the liquid underneath the piece of platinum, so that this electrode is wetted by the gas. Such a cell is regarded as if it had been a "metallic hydrogen" electrode in the solution of one-normal hydrogen ions. The electromotive force series indicates the normal potential for reduction and oxidation reactions when, for instance, one metal is transformed into the state of ions. In a solution containing one mol. of the ions per litre, the normal potential for the reaction $Fe \rightleftarrows Fe^{++}$ is found when we examine the potential difference between an iron electrode in a uniform iron ion solution on one hand and a hydrogen electrode of the construction mentioned above on the other hand. The liquid phases of the two half-cells are combined by a salt water bridge. If an iron electrode is placed in a liquid different from the uninormal Fe^{++} solution and this medium is combined through a salt water bridge with the hydrogen electrode, we will observe a potential of the iron which is different from the normal potential. This potential against the hydrogen electrode is called E_H for the iron. Very often we use reference electrodes other than the hydrogen electrode. This only means that we have to add or subtract the constant value from the potential measured in order to obtain the E_H.

In corrosion techniques a so-called coppersulphate reference electrode frequently is used instead of the standard hydrogen electrode. It is therefore fairly common to find references to the potential of a given object in a corrosive medium stated in mV, often omitting the reference electrode. This may lead to confusion, as the physical chemist normally will consider such stated values identical with the E_H value. However, corrosion engineers may mean by the potential value the value against the copper-sulphate electrode. As seen from the table below, the standard electrode potential of copper against one normal Cu^{++} is 345 mV higher than H_2/H^+ electrode. References given to a copper-sulphate electrode therefore will have to have subtracted a constant value of 345 mV in order to give the E_H value. This constant, however, refers to a system of chemically pure copper in a uni-normal copper ion solution. In practice the copper sulphate electrodes are constructed from an ordinary electrolyte copper wire in a saturated solution of copper sulphate. As the copper sulphate $CuSO_4 \cdot 5H_2O$ has a molecular weight of 250, whereas the solubility of copper sulphate in water varies between 316 g per litre at 0° C and 2 033 at 100° C, the potential of a copper electrode in saturated copper sulphate will be somewhat lower than the standard potential according to Nernst equation (see page 5). However, as the variation in concentration of copper corresponding to a power of ten only gives a deviation of about 28 mV at normal temperature, the deviation between the standard potential and the potential obtained by the normal copper copper-sulphate electrode will be quite insignificant. In practice the reference electrode is constructed in the following way:

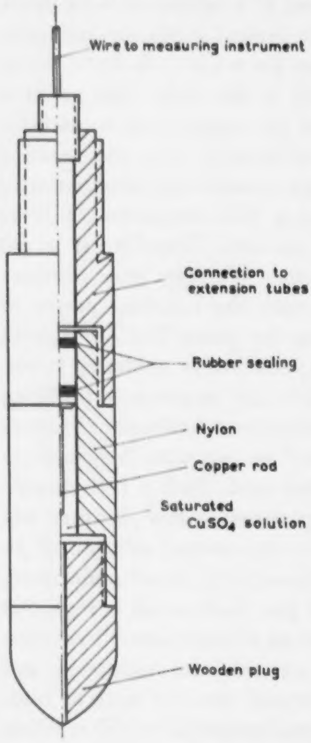

Fig. 10. Copper/copper-sulphate standard electrode as used by the Norwegian Geotechnical Institute as a reference potential.

A copper wire is lead watertight into a very thick-walled tube of perspective glass or some other insulting material, in the end of which is fitted a stopper of hard wood which may be screwed into the tube. Before use the tube is filled with a saturated solution of copper sulphate, and the stopper screwed tight into the tube. This hard-wood stopper acts as a semi-pervious membrane, allowing the charged ions to pass whilst the flow of liquid is hindered. When the potential of a steel pile is to be measurd, such an electrode may be pressed down in the ground by means of extension tubes, whilst the copper wire from the electrode is continued by a cable through the tube up to the ground (see Fig. 10).

The potential differences which arise between different electrodes when no electric current flows in the system are collected, under normal conditions, in the electromotive series, using the reaction $H_2 \rightleftarrows = 2H^+ + 2e^-$ as reference point. For the most important metals this electromotive force series is given in Table 1.

TABLE 1

Electrode Reaction	Standard Electrode Potential, E_0 (Volts) 25° C	Electrode Reaction	Standard Electrode Potential, E_0 (Volts) 25° C
$K = K^{+} + e^{-}$	– 2.922	$Ni = Ni^{++} + 2e^{-}$	– 0.250
$Ca = Ca^{++} + 2e^{-}$	– 2.87	$Sn = Sn^{++} + 2e^{-}$	– 0.136
$Na = Na^{+} + e^{-}$	– 2.712	$Pb = Pb^{++} + 2e^{-}$	– 0.126
$Mg = Mg^{++} + 2e^{-}$	– 2.34	$H_2 = 2H^{+} + 2e^{-}$	0.000
$Be = Be^{++} + 2e^{-}$	– 1.70	$Cu = Cu^{++} + 2e^{-}$	+ 0.345
$Al = Al^{+++} + 3e^{-}$	– 1.67	$Cu = Cu^{+} + e^{-}$	+ 0.522
$Mn = Mn^{++} + 2e^{-}$	– 1.05	$2Hg = Hg_2^{++} + 2e^{-}$	0.799
$Zn = Zn^{++} + 2e^{-}$	– 0.762	$Ag = Ag^{+} + e^{-}$	0.800
$Cr = Cr^{+++} + 3e^{-}$	– 0.71	$Pd = Pd^{++} + 2e^{-}$	0.83
$Ga = Ga^{+++} + 3e^{-}$	– 0.52	$Hg = Hg^{++} + 2e^{-}$	0.854
$Fe = Fe^{++} + 2e^{-}$	– 0.440	$Pt = Pt^{+++} + 2e^{-}$	ca. 1.2
$Cd = Cd^{++} + 2e^{-}$	–0.402	$Au = Au^{+++} + 3e^{-}$	1.42
$In = In^{+++} + 3e^{-}$	–0.340	$Au = Au^{+} + e^{-}$	1.68
$Tl = Tl^{+} + e^{-}$	– 0.336		
$Co = Co^{++} + 2e^{-}$	– 0.277		

The more negative the electrode potential, the more unnoble is the metal. One chemical reaction involving a more negative reaction than another will pass from the left to the right, whereas the other reaction will pass from the right to the left, if two such electrodes are coupled together. If for instance a piece of metallic iron is placed in a solution of bivalent copper salt, the iron will dissolve, whilst the copper will be precipitated in a metallic state. In this way the iron object may be covered with a film of copper simply by dipping it into a solution of copper sulphate. This is seen clearly from the reaction pair $Fe = Fe^{++} + 2e^{-}$, standard potential – 0.440 Volt and $Cu = Cu^{++} + 2e^{-}$, standard potential + 0.345 Volt. In a corresponding way copper may precipitate silver from a silver solution, and platinum precipitate gold from a gold solution. The electromotive force series is only valid for metals in given concentrations of their own salts. In other electrolytes, as for instance in soil, the precipitation/corrosion series will be different, and it is not possible to give exact values for the difference in potential for reactions. However, the rule shown to the right, which is based on experience, will normaly be valid.

The three metals in the upper part of this series normally will corrode in soil to such a degree that they may be used for galvanic protection of steel and iron. This is treated in a later chapter.

The relative position of the various metals in different media may vary from case to case, depending upon the composition and the oxidizing power of the environment. By comparing the voltage between a given metal and the steel electrode in the ground it is possible to get the numerical value for the difference in red-ox potential of the

Empiric galvanic series of metals and alloys in sea water and soils:

Magnesium
Zinc
Aluminium
Carbon steel
Alloy steel
Cast iron
Brass
Red Bronze
Copper
Special Bronzes
Copper-Nickel Alloys
Nickel
Silver
Stainless steel
Monel
Titanium

given metal's corrosion reaction compared with that of steel. However, we may like a numerical expression to refer to without using steel or iron as the one electrode. Such a value will be of more universal interest. We may compare the potential of platinum placed in the medium against the hydrogen electrode or any other steel electrode. The difference in potential between the platinum electrode and the hydrogen electrode when no current passes in the system is commonly designed E_h to mark the difference from E_H. In some literature E_h is called the red-ox potential of the medium, so that negative values refer to the medium which is normally considered to be the reducing agent, whereas high positive values expressed in volts or millivolts are found in liquids which normally are considered oxidizing. Whether a substance is an oxidizing or reducing agent, however, depends upon which reactions take place. Even liquids with a high negative E_h value may act as oxidizing agents on metals such as the alkali metals. Such liquids may cause cathodic depolarization by corrosion. To call E_h the red-ox potential of the surrounding medium is not fully correct, as the red-ox potential is an expression for a certain reaction, and not an expression for a substance. The expression E_h, however, has entered into a whole group of literature, and probably we will never get rid of it again, although it would be advantageous to clarify the expressions and bring them into a more exact state. In biology, for instance, the expression E_h is used as an expression for the reducing power of the culture medium.

CHAPTER III

PASSIVITY - IMMUNITY - INHIBITION - OVERVOLTAGE

a. Passivity.

When a metal object is placed in an electrolytic liquid, an anodic and a cathodic area arise spontaneously, and an electric current flows in the system. The magnitude of this electric current may vary from insignificant values to many amperes per sq.m. When a current flows it is not possible to measure the reversible potential in this corrosion-active state. Between the thermodynamic and the measureable potential there is the relation $E_f = E_m + f(i)$. Here $f(i)$ is a function of the corrosion current which arises as a result of the local elements. For the simplest corrosion process in aqueous solutions the following reaction occurs at the cathode: $Fe \rightleftarrows Fe^{++} + 2e^-$, and at the anode $2H^+ + e^{--} \leftrightarrows H2$. The rate of reaction and consequently the magnitude of the corrosion current depend upon many factors: at the cathode we have overvoltage and depolarization, at the anode we have solution of the iron ions and anode depolarization. Anode and cathode potential depend upon the alloying substance, which in normal mild steel is carbon, silicon, manganese, phosphorus or sulphur. The action of all these factors together with other chemical and mechanical states gives different corrosion potentials in different corroding media and for different chemical, mechanical, and thermal states. Fig. 11 shows the change in anodic and cathodic potential as a function of the corrosion current. E_a represents the reversible potential, and E_k the cathodic potential corresponding to the liberation of hydrogen. E_1 and E_2 are measureable corrosion potentials (steady state potentials) giving the measureable state between the two extreme values. When *p*H decreases, the potential of the cathode and the polarization curve of the cathode change in cathodic direction. This gives a shift in the corrosion potential E_2 towards cathodic potential. For increasing corrosion current and decreasing *p*H there will be a steady incrase in the corrosion potential. In all active corrosion processes the corrosion potential is of the greatest importance, as its value indicates the velocity of corrosion. The relation between *p*H and steady state electrode potential was given by M. J. N. Pourbaix in 1949. The diagram Fig. 12 is a simplified variety of the well-known Pourbaix diagram. From this diagram it

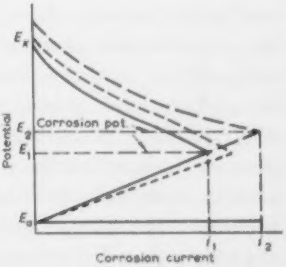

Fig. 11. The shift in anodic and cathodic potential as a function of corrosion current.

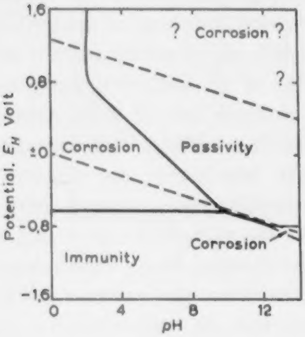

Fig. 12. Simplified Pourbaix diagram for the system FeH_2O.

is seen that the potential *p*H space may be divided into three separate parts, the immune area of the protected area, the active corroding area and the passive area. In order to understand the corrosion of reinforcement steel in concrete, the Pourbaix diagram is of the greatest importance when interpreted the right way. As we will see, at a given *p*H value, about 9.5, steel will be either in a passive area or in an immune area. As the *p*H value in normal noncarbonatized concrete generally is of the order of 12, it must be expected that reinforcement steel for normal potentials will be in the passive area. The concept of passivity is still the subject of important discussion, and a fundamental theory for the passivity which is able to explain all observed phenomena has not been proposed as yet. According to a hypothesis by Håkon Nord (1958) steel in an aqueous medium may represent three different states. We arrive at this conclusion when we start by supposing a continuous monomolecular layer of adsorbed water on the surface of the metal. In the immune state, i.e. for a sufficiently low E_H value, this layer of water is not dissociated. Thus the oxygen atom in the monomolecular layer is adsorbed into the metal atoms or the electrons in the metal, forming metallic bonds between the chemisorbed water in the metal. The two hydrogen atoms for each oxygen point away from the metal surface. In the corrosive-active areas one hydrogen is dissociated from the water so that the surface is covered with a monomolecular layer of OH. If the potential is lowered from this state, hydrogen ions from the surrounding medium are attracted, and the protected immune state is re-established. If the potential is increased, even the second hydrogen atom may be dissociated from the original water molecule. Consequently the metal surface becomes covered by a continuous layer of oxygen. We call this either a chemisorbed layer of oxygen, or a continuous two-dimensional layer of iron oxyde. The difference between those two opinions does not seem to be great. In the passive area the steel is corroding at an immensely slow rate. For certain steel alloys it will be easy to arrive in the passive area, and special precautions are to be taken in order to bring the steel into the active area. Such steel is called stainless steel. Normally it is not used in construction as foundation piles or as pipe lines, or for other objects placed in soil. For the mild carbon steels the border between the active and the passive areas is no mathematical line. It depends to a great extent upon the composition of the steel, but to a still higher extent upon the composition of the surrounding medium. For instance W. J. Copenhagen (1958) and co-workers have shown that the potential for transmission from passive to active at a given *p*H is much higher in a chloride-bearing medium than in a medium which is poor in chloride. Our marine clays normally will have considerable amounts of chloride present, and the only concrete constructions which will have chloride concentrations so high that the border line between active and passive areas will be shifted markedly towards higher values are those which in the winter use calcium-chloride in the water. The consequence is that there may be active corrosion at higher *p*H values than normal. This is seen from the Pourbaix diagram if a line is placed above the given border line between passive and active. It is worthwhile to remember that the velocity of the corrosion at a given *p*H does not depend upon the difference between the potential which causes the passivity and the potential which causes immunity. This difference is small at *p*H 8–9.5, but nevertheless, even at such *p*H values the corrosion may be more rapid than at, say *p*H 4. This depends upon many factors, mainly the cathodic depolarization.

Passivity is in itself not a very good protection against corrosion of normal steel. It may be broken easily on parts or the whole of a steel surface, and rapid corrosion may arise. Immunity, however, is a very good protection against corrosion. This may be created for steel by using so-called cathodic protection, which means lowering of the potential, whereas passivity will arise naturally at several *p*H-values and may be produced by anodic protection. In such cases, however, we will often have transitions from the passive to the active state, and active corrosion will arise.

For concrete piles or other concrete constructions in soil we may have localized carbonatization through thin cracks or on smaller spots. The local *p*H value may then decrease below 9.5, which may bring the steel into the active area with an unfavourable distribution of the areas for cathode and anode. This may lead to a quick deterioration of the reinforcement steel, and as formation of rust is often involved, expansion due to the corrosion products may be very harmful to the covering concrete. Thus it is a common experience that reinforced concrete stands up less well to sea water than does concrete with no reinforcement. This is due to the fact that chemical attacks by sea water act simultaneously upon the concrete and the reinforcement steel. The swelling due to the rust opens the cracks in the concrete, permitting sea water with its harmful agents to enter the concrete to a greater extent than would have been the case if no steel had been present. In this case we must be aware of the fact that *p*H values below 9 may occur easily in concrete which reacts positively on a normal phenolphthalein test, although the phenolphthalein is colourless below *p*H values of 10.2. In a broken piece through the concrete new spots which are not carbonatized will be exposed, and calcium silicate minerals will be hydrated if water is added, consequently reacting by giving a high *p*H value and a positive phenolphthalein reaction. Nevertheless, the concrete may be carbonatized down to harmful low *p*H values along cracks, and the cement hydrate minerals which have not reacted occur as armoured relics.

b. Immunity.

As seen from the Pourbaix diagram, steel may shift into the immune state when the potential is lowered below a certain borderline, which depends relatively little upon the *p*H value. Such a lowering of the potential may take place when the metal in the corrosive medium is subjected to a current of electrons somewhat larger than that normally consumed by the cathodic depolarization process. In principle it is unimportant from which source these electrons are delivered. They may originate through the corrosion process taking place on another metal which is shortcircuited to the steel, provided this other metal has a lower corrosion potential than the steel in the same medium, i.e. provided the other metal is less noble than the steel. In other cases the electrons may be delivered from an external source of electricity. The first-mentioned method is called the method of sacrificing anodes. It has been known and employed for a long time for different metallic covers. Sir Humphrey Davy (1824) was the first to propose using zinc blocks fastened to the coppers of the British Naval ships. The modern zink covering, which is called galvanization, is a well-known technical process. Here the zinc acts as a protective in two ways. First, the zinc forms a continuous cover over the steel. and protects itself from rapid corrosion by a cover of zinc oxide or hydroxide. Second, the zinc lowers the potential of the steel. In this way even places where the zinc cover has been scratched off and the steel is in direct contact with the corrosive medium will not suffer corrosion, because they cannot form anodes. This means that, due to the zinc which is short-circuited to the steel, the potential of the steel is so negative that positively-charged iron ions cannot leave the steel surface. In practice the use of a less noble metal as a protection is very common, especially in the shipping industry. External as well as internal so-called sacrificing anodes of magnesium alloy or high purity zinc today are installed to a great extent, especially in the case of tankers. The corrosion in cargo tanks costs enormous sums. During return trips some of the tanks have to be filled with sea water as ballast, and at the high temperatures which are normal in such tanks the very corrosive sea water may attack the plates of the tanks severely. In most modern ships zinc or magnesium anodes are bolted to the steel plates of these cargo tanks. These anodes corrode themselves, supplying sufficient electrons to keep the steel potential low enough to bring the steel into the immune areas of the Pourbaix diagram. This is the reason for the name "sacrificing anodes." The corrosion of these unnoble metals is sufficiently rapid to provide the necessary number of electrons, so that only a small fraction of them are used on local cathodes at the surface of the unnoble metal. These unnoble metals have no other effect than providing the current.

It may seem uneconomic first to produce the magnesium metal by electrolysis of magnesium salts in a factory, and then to use the magnesium metal in the corrosion process, where it returns to magnesium salts, in order to liberate the same amount of electricity. A direct supply of electrons from an electric rectifier is undoubtedly a great advantage, but mostly it is not used in tanks because of the danger of explosions due to sparks which may develop in a tank where explosive gases can never be excluded. For other constructions, for instance pipe lines and foundation piles, there is no need to take this precaution, and the potential of the construction may be lowered from an external source. It is, of course, an economic question, as the application of an external source for electricity most often involves high costs of installation. On the other hand, maintenance costs are low, whereas the application of unnoble metals as sacrificing anodes involves low costs of installation, but higher costs of maintenance. As the cost of installation will be relatively higer for small constructions than for larger ones, it may be rational in some cases to use sacrificing anodes when only a few piles are involved, whereas external sources will normally be most economic for larger buildings. The cost of labour, the cost of electricity and other economic factors of course will change from place to place, and no definite size can be given at which the one or the other of the methods is to be recommended. As both methods involve extra costs, however, it is necessary to clarify in advance the velocity of the natural corrosion which will attack the construction. The calculated life must be compared to the time for which the construction is intended to last. In most housing and factory buildings no external electric corrosion protection will be necessary in ground where the corrosive power is moderate, as such buildings normally are not intended to last for more than 50–150 years. For churches, town halls, and other such buildings, corrosion protection must be installed in soils where it can be omitted in the case of a factory. As localized corrosion may be more dangerous the more extensive the construction, we will find normally that pipe lines are more subjected to localized attacks than foundation piles or sheet piles. Consequently, it will often be an advantage to attach galvanic protection to pipe lines, even though such installations can be omitted in the same ground in the case of foundation piles.

c. Inhibitors.

Another method to slow down the corrosion process is the use of so-called inhibitor processes. These processes have been regarded mainly as some kind of a chemical covering of the metal surfaces involved. It has been known for a long time that several chemical compounds may slow down or inhibit the corrosive power of media otherwise considerably corrosive. If, for instance, a solution of sodium chromate is added to a brine, this becomes far less corrosive to steel than if it had been free from chromate (Fig. 13). A long series of organic compounds behave in a similar manner. The most natural hypothesis, of course, is to assume that the chromate or the organic compounds form an extremely thin film of reaction products, covering the steel surface in the same way as painting or enamelling, or covering by a noble metal. However, the processes collected under the term "inhibition" are of a more complex nature. In a later chapter bacterial corrosion and criteria involved in the corrosion of antiquities are dealt with. Here it may be mentioned that tan from oak planks in the Viking ships, and tanned leather and other rubbish, together with phosphate solutions from corpses and sacrificed animals, have acted as protection against corrosion. In other cases it may be demonstrated that minute amounts of chemical compounds may decrease the velocity of corrosion effectively even where the amounts of chemical compounds are so minute that they have not formed a continuous monomolecular layer of any compound on the metal surface. In such cases it seems as if the inhibitors act by blocking "active spots" on the corroding steel crystal. It is well known that all real crystals deviate from the ideal crystal because of crystallographic "errors" in the surface, as for instance *Schottky* or *Frenkel* defects.[1] At such spots the activity of the metal atoms is higher than average. For instance, colloidal chemistry has shown that the heat of wetting found when a crystal is wetted by a liquid is much higher for the first traces of the liquid than the heat developed by the same amount of liquid when the greater part of the surface is already wetted. This is explained by assuming that the heat of reaction (heat of wetting) per molecule of liquid depends upon whether the liquid is adsorbed at an active, i.e. a disordered, spot or on a perfect crystalline part of the metal surface. For such, and other, reasons therefore we have assumed that the corrosion processes start at especially active spots on the metal surface where some kind of crystallographic defect is present already, and that the further process of solution takes place one

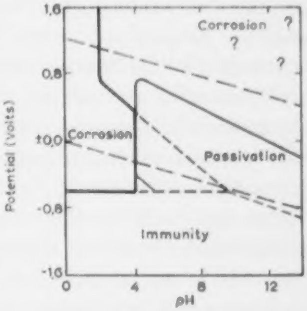

Fig. 13. Domains of corrosion immunity and passivation for iron in presence of chromate (solution containing 155 g K_2CrO_4 and 3.5 gCl^- per l). (After Pourbaix).

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[1] Schottky and Frenkel defects are lattice defects leaving ionic or metallic crystals electrically neutral. Descriptions of these types of lattice defects may be found in any encyclopedia of science or chemistry.

atom after another from these active spots to all sides of the crystal, so that the crystal lattice deteriorates in a way analogous to a lady's stocking in which there is a hole at one place. The process of inhibition could be compared to the treatment in such a case. It seems to be practice to put a drop of nail varnish on the hole in order to prevent laddering. It is not necessary to dip the whole stocking into varnish. However, recent investigations seem to indicate that the inhibition process cannot be explained by such a simple picture. It is not only that the inhibitor forms an insoluable precipitant on the active spots. G. A. CARTLEDGE demonstrated (1955, 56) that the artificially radioactive element, technetium, in a hepta-valent state as the pertechnetate ion TcO_4^- has a quite unusually good activity as inhibitor, much greater even than that of the chromate ion CrO_4^{--}. As technetium is radioactive, it was easy to show on a photographic film where the technetium had precipitated on the metal surface. From this experiment it was seen that the amount of technetium precipitated varied from sample to sample, and that the amount of precipitants was much less than necessary to form a continuous film. Further, it was found that the amount of technetium on the steel surface did not increase with time, even in solutions relatively rich in technetium, where the possibilities for increasing amounts of iron-technetate should be present. Pieces of metal which had been kept in solutions of pertechnetate for periods as long as three years did not increase in radioactivity. However, if other ions, as for instance the sulphate ions, were added to the solution, it could be observed that the technetate ion was liberated from the metal surface, and corrosion started. In this way it could be demonstrated that quick oscilliations occurred in the electric potential of the metal. This easy replacement reaction indicates that the forces which keep technetium bound to the metal surface are weaker than the normal chemical bonds. Cartledge interpreted these results by assuming that the hepta-valent positively charged central atom in the tetrahedral cage of oxygen could be displaced easily from the centre of the TcO_4^- ion. In this way it could be electrostatically attracted by the electrons on the metal surface, blocking them from entering the partial reaction which is necessary to fulfill the process of corrosion. Fig. 14 shows CARTLEDGE's (1957) model.

In usual systems, as for instance steel piles in soil, we cannot hope for passivity, immunity or special inhibitor actions. The reason why the corrosion of steel in soil does not take place at a much higher velocity, as we should expect from the great differences in free energy between the initial and the final states, is mainly the slow cathodic depolarization process, and partly the slow diffusion of oxygen towards the cathodes or the diffusion of hydrogen away from the cathodes. These processes are dealt with in a later chapter.

d. Overvoltage.

In any case where an electro-chemical process takes place with a measureable velocity, the process is only possible by a deviation from the equilibrium conditions. For instance, in electrolysis of an aqueous solution of an electrolyte, hydrogen may develop at the cathode. This means that the cathode becomes covered by an atomic or molecular layer of hydrogen. Thus the cathode changes its character. By equilibrium conditions we understand the state where the neutralization of positively-charged hydrogen ions and the reverse process, which is the formation of hydrogen ions, have the same velocity.

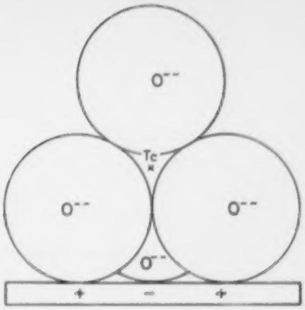

Fig. 14. Cartledge's model.
The architecture of the pertechnetate ion (TcO_4^-) is believed to be responsible for its corrosion-inhibiting properties. The ion consists of a technetium atom (Tc) with four oxygen atoms (O) arranged around it in a tetrahedron. (The cromate and sulphate ions have the same structure) The valence electrons of the technetium atom give it two negative charges (−−). The distribution of these charges may be such that the core of the ion is positive and attracts negative electrons on the surface of iron. This would immobilize the electrons to some extend and block corrosion. (After Cartledge).

Under such conditions it is a matter of course that no current will pass in the system. For any potential we have a state of equilibrium, which depends upon the concentration of hydrogen ions in the liquid phase and partially upon the pressure of hydrogen gas above the liquid. The hydrogen gas develops at the electrode, and the liquid phase in the neighbourhood of the electrode is rendered more alkaline due to the consumption of the hydrogen ions. For various metals the voltage necessary to produce the development of gas at any measureable rate varies considerably from the equilibrium state for no development of gas. This deviation from the equilibrium depends upon the current density. An analogous deviation is found for anodic processes, for instance by electrolysis of water, where oxygen is developed on the anode and hydrogen on the cathode. The sum of the deviations of anodic and cathodic potentials from the equilibrium state is called overvoltage. The magnitude of the overvoltage depends upon the nature of the electrode metals, and is of importance for corrosion reactions when different metals are coupled in a corrosion cell. Overvoltage acts in slowing down all technical corrosion processes. The importance of overvoltage in technical corrosion is dealt with thoroughly by G. V. Akimov (1958).

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CHAPTER IV

A SURVEY OF SULPHATE-REDUCING BACTERIA AND ANAEROBIC CORROSION BY MICROBES OF IRON

after Emmy Egidius Möllerud (1960).

a. Sulphate-reducing bacteria, their occurrence, growth conditions etc.

The reduction of sulphate into sulphide can be done by a small group of bacteria only, but in return this group has a very wide distribution. The sulphate-reducing bacteria are placed systematically in one genus, *Desulfovibrio* of the Pseudomonadaceae family. In *Bergeys Manual* for 1948[1] the genus *Desulfovibrio* is registered with three species, *D. desulfuricans*–a species which is common in soil and fresh water, *D. aestuary*–which is found in sea water and marine sediments, and *D. rubentschikii*–which also is found in soil and fresh water and which differs from *D.desulfuricans* in that it can attack higher fatty acids. But these three species are so uniform, both morphologically and physiologically, that they can be discussed together here. To avoid mistakes it may be mentioned also that *D.sulfuricans* in earlier literature is referred to under the following synonyms: *Bacterium hydrosulfureum ponticum, Spirillum desufuricans, Bacillus desulfuricans, Microspira desulfuricans, Vibrio desulfuricans,* and *Sporovibrio desulfuricans.*

The sulphate-reducing bacteria have a wide distribution. They have been found in soil, fresh water, sewer water, mineral water sources, sea water, marine bottom samples and sediments, in stone formations, oil wells and so on, from different geographical areas and under greatly varying conditions. For example: They have been found in clay samples down to 70 metres depth in northern Holland, in samples of water and oil from oil wells down to 120 to 570 metres depth in Illinois, in samples down to more than 900 metres in oil wells in California, and also in samples taken from the great depths of the ocean. The decreasing concentration of sulphate and the increasing concentration of sulphide with geological age in marine sediments indicates that the sulphate-reducing bacteria are active *in-situ.*

Normally the sulphate-reducing bacteria are short, slightly bent bacilli. They are mobile with a polar flagellum and are Gram negative. In older substrates and in substrates cultivated under "unusual" conditions, for example high temperature, they also occur in uncommon forms.

The sulphate-reducing bacteria demand anaerobic conditions; oxygen does not actually kill them, but when it is present they are unable to develop. Their respiration thus is inter-molecular and they grow best in reducing surroundings optimum at $E_h = -0,2$ to 0,3 mV. They can grow in neutritive media with E_h up to + 0,4 mV, but the potential then decreases rapidly down to about − 0,3 mV during growth.

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[1] *Bergeys Manual of Determinative Bacteriology* is the most important hand-book in bacteriology, the last issue hitherto dating back to 1948.

Desulfovibrio are the only bacteria hitherto known which bring about the reduction from sulphate to sulphide. The sulphate acts as the specific hydrogen acceptor during the oxidizing of the materials attacked by the bacteria. These bacteria are unable to develop when no sulphate, or one of the few materials which can substitute for it, is present. Sulphate can be substituted by sulphite, which probably also is formed as an intermediate product during the sulphate reduction, and by thiosulphate, which is not reduced as easily as sulphate and sulphite. Some orders may also use fumarat instead of sulphate. As the hydrogen donor some simpler compounds such as primary alcohols and simple carbohydrates can be used. The materials which are attacked vary somewhat from one species to the other. A great part of the order also is able to use molecular hydrogen for the sulphate-reducing process.

A great part of the sulphate-reducing bacteria can develop autotrophically, i.e. they build up their metabolism from simple, inorganic compounds. Thereby they get their energy supply from the oxidation of molecular hydrogen and their requirement for carbon from carbonate or CO_2. The autotrophic growth is not very effective, the reduction of sulphate giving:

$$H_2SO_4 + 4H_2 \rightarrow H_2S + 4H_2O + 56{,}75 \text{ cal.}$$

The growth in heterotrophic media is far richer. Since the autotrophic growth depends upon sulphate reduction by molecular hydrogen, only the species with the specific dehydrogenase are able to develop under such conditions. The hydrogenase seems to be an adaptable enzyme since species which "originally" are unable to oxidize hydrogen can become accustomed to using it. The hydrogen need not be added to the substrates as such. A sufficient amount is formed by adding metallic iron to the medium.

The H_2/H_2S ratio during autotrophic growth is larger than the theoretical 4, which would mean that the hydrogen was oxidized quantitatively to H_2S and water. The larger ratio means that hydrogen also is consumed for the reduction of CO_2 in the cell's synthesis of organic material.

The sulphate-reducing bacteria are very resistant to H_2S, which in active substrates can be formed in amounts reaching 1500 mg/l. The halophile (i.e. requiring saline conditions) marine species reduce sulphate quicker than the non-halophile.

The sulphate-reducing bacteria grow best between pH-values from 5,0 to 9,0, at the neutral point.

The sulphate-reducing bacteria originally were isolated at about 30° C. Subsequently, species have been isolated at 55° C. It has been shown that species originally isolated and cultivated at 30° can become accustomed to grow at 55° and vice versa, if only the "acclimatization" is made step-wise and the steps are not too large. The optimum temperature for the greater part of the orders lies between 28° and 38° C. It seems to be dependent upont the temperature conditions at the place where they are found. Orders isolated from marine sediments where the temperature was about 40° C had a growth optimum at this temperature. It seems as if these bacteria easily can become accustomed to grow at temperatures other than the "normal" one. On a whole the sulphate-reducing bacteria seems to become easily accustomed to new conditions, conditions which–if they are allowed to last–finally will be of vital importance for the bacteria. As an example may be mentioned an order which was isolated from marine bottom samples taken at great depths; this order was unable to develop unless it was kept under a pressure of approximately 600 atm.

The sulphate-reducing bacteria are very resistant to ordinary disinfectants such as phenol, cresols, chlorine etc., and likewise to the most usual antibiotoca. Penicillium and streptomycin have no effect at all, auromycin, chloromycin, and neomycin cause a weak resistance. However, the existence of another antibioticum, hitherto unclassified, which prevents the sulphate-reducing bacteria from attacking iron in soil, has been proved. Further, it has been found that selenate, mono-fluorophosphate, tannate, and potassium-bichromate have a strongly preventative effect. Selenate and mono-fluorophosphate probably have an effect because of their structural similarity to sulphate; their effect depends upon the amount of sulphate present. Neither has any effect upon the reduction of sulphite or thiosulphate. Tannate and K_2CrO_4 seem to have another functioning mechanism, as the effect of these materials does not depend upon the concentration of sulphate. The effect of similar materials such as tellurite and selenite has also been tested, but they had little or no effect.

b. Occurrence of sulphate-reducing bacteria in Norway.

The wide distribution of the sulphate-reducing bacteria elsewhere in the world means that there is no reason to believe that they should not be common in our country also.

Although we seem to be bothered by their attacks on iron constructions in soil to a very small degree, this hardly is due to their neutritive demand. They require reducing surroundings; *p*H at about the neutral point, sulphate and a trace of iron. They grow in autotrophic media when, apart from this, carbonates or CO_2 and hydrogen, K, Na, NH_4, Mg, Cl, and PO_4 are present.

They grow better when some organic material is present, and far from all the orders are able to grow purely autotrophically.

The bacteria are restrained, among other substances, by selenate, tannate, and one or more antibiotica, which in certain places are developed by Actino-mycetes. However, this does not explain their failing or insufficient development otherwise than purely locally.

When looking at the sulphate-reducing bacteria's wide distribution one has to believe that they are capable of developing also at temperatures far below optimum (about 30° C). Two cases are referred to, describing investigations with 18–20° as the lowest temperature. These investigations proved that the reduction was considerably slower at 20° than at the optimum; in one of the cases the figures were 24 % reduction and 36 % reduction respectively. That the metabolism is slower at a lower temperature is only to be expected, but how much it decreases at, for instance, 5–10° C (which represents our normal soil temperature) is not known.

c. Anaerobic corrosion by microbes of iron in a neutral soil.

To-day it seems to be recognized commonly that the sulphate-reducing bacteria play an important role in the anaerobic corrosion of iron in a neutral soil. The corrosion process is usually explained electro-chemically, as stated earlier; therefore, no noticeable corrosion of iron in a neutral, non-oxidizing soil should occur. When, in spite of this fact, corrosion occurs, it must be due to the fact that the depolarization can take place otherwise than by means of free oxygen. In 1934 V. Wolzogen **Kühr**[1] presented a theory, stating that the sulphate-reducing bacteria which can oxidize molecular hydrogen by means of oxygen separated by a reduction of sulphate are the real cause of the metal depolarizing, and the corrosion may continue under anaerobic conditions. According to this theory the corrosion process may be summed up in the following equation:

$$4Fe + 8H^{+} \rightarrow 4Fe^{++} + 8H$$

The reduction of sulphate into sulphide, which is believed to take place step-wise, may be summed up in an equation which shows the depolarization of the metal:

$$H_2SO_4 + 8H \rightarrow H_2S + 4H_2O$$

and the corrosion products are:

$$Fe^{++} + H_2S \rightarrow FeS + 2H^{+}$$

$$3Fe^{++} + 6OH^{-} \rightarrow 3Fe(OH)_2$$

The total red-ox equation then is:

$$4Fe + H_2SO_4 + 2H_2O \rightarrow 3Fe(OH)_2 + FeS$$

This theory is now adopted by most scientists working within this field and furthermore is supported by the facts outlined below.

In most cases concerning corrosion of iron in neutral, anaerobic soils, the soil layer next to the metal is found to be definitely black. Further, very often a crust, many centimeter thick is formed. The black colour originates from the formation of FeS, which is one of the corrosion products. Upon exposure of a corroded article the black colour disappears rapidly as the sulphide oxidizes. If some time elapses between the excavation and the investigation, this fact often leads to an incorrect diagnosis of the corrosion source.

The corrosion products always large amounts of sulphate-reducing bacteria and the number of bacteria always seems to be greater close to the surface than a few centimeters away from it.

Repeated corrosion experiments in the laboratory show that iron and steel are attacked in the same way as by corrosion in neutral, anaerobic soil when placed in active substrative of sulphate-reducing bacteria. To the contrary, in pure substrate media the metal is not attacked at all. The sulphate-reducing bacteria grow even more quickly when a piece of iron or steel is added to the substrates. The sulphate-reducing bacteria contain an enzyme which is capable of catalyzing the reduction of sulphate by means of molecular hydrogen. The sulphate-reducing bacteria also are able to grow in pure inorganic solutions. In such cases they use the reduction of sulphate–the oxidation of molecular hydrogen–to cover their requirement for energy. In such cases the hydrogen does not even have to be added as such; it is sufficient if a piece of metallic iron is put into the saline solution.

The corrosion of iron, mainly cast-iron and steel, is probably the only corrosion process of any importance, but it has been shown experimentally that other metals such as lead, copper, aluminium, and zinc can be attacked in the same way.

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[1] See References on anaerobic bacteria and bacterial corrosion, p. 33.

Theoretically also other anaerobic, bacterial reduction processes such as reduction of nitrate, carbon dioxide and phosphate may cause corrosion in the same way as the reduction of sulphate. In any case the corrosion product will be $Fe(OH)_2$. The reduction of CO_2 into methane performed by the so-called methane bacteria often takes place parallel to the sulphate reduction. By carrying out laboratory investigations on both kinds of bacteria, however, it is shown that no gas is evolved, which indicates that the sulphate-reducing bacteria are rampant during the corrosion process, because these bacteria are unable to adsorb methane. Consequently there is no reason to believe that no reduction process other than the sulphate-reduction plays any important role in corrosion in nature.

The bacterial sulphate-reduction is not only responsible for the corrosion of iron in anaerobic neutral soil. The corrosion product FeS in itself is active towards metallic iron, as are materials such as pyrite, ferrisulphate, and primary sulphur, which is formed by oxidation of FeS. When corrosion takes place in areas where the conditions vary between anaerobic and aerobic, for instance during long dry periods, the FeS formed will be oxidized easily into the compounds mentioned above. Also, the primary reduction product H_2S attacks iron and may be active parallel to the depolarization of the bacteria. The fact that the ratio Fe/FeS–where Fe is totally corroded iron and FeS is iron shown as sulphide–proves that the H_2S formed is not the direct cause of the corrosion. If H_2S had been the real cause of corrosion, all the iron corroded would necessarily be retrieved as sulphide, the ratio Fe/FeS having to be 1. From the reaction equation concerning the corrosion process, the ratio theoretically is 4. In practice, however, it is always found to be somewhat lower, viz. between 2.5 and 3.5. This probably is due to the fact that during the growth of the bacteria a constant oxidation of organic material takes place, at the same time also forming some H_2S, so that more FeS is formed compared with the equation concerning the corrosion process. In practice, therefore, the ratio has to be lower than 4.

Of course an attempt has been made to prove whether it is possible to find some correlation between the complexity of soil, especially its content of sulphate and carbon, measurable soil properties such as pH, E_h, moisture equivalent and so on, and the degree of corrosion. Such a correlation has not been found. The safest measurable factor to indicate whether an area is corrosive or not is the red-ox potential when pH does not differ too much from the neutral and the soil has a reasonable content of sulphate. From the values of the red-ox potential a certain indication of the degree of corrosion to be expected in a definite area can be drawn from the following scale:

E_h more than 400 mV – no corrosion
E_h 200–400 mV – weak corrosion
E_h 100–200 mV – moderate corrosion, and
E_h below 100 mV – strong corrosion

From pH and E_h measurements in 48 test fields the correct degree of corrosion could be predicted in about 67 % of the cases; the remaining 23 % of the cases differed more or less from what could be expected. That the degree of corrosion differs in some of the cases from what can be expected is only normal, because as mentioned before, other factors than the sulphate-reduction are active during the corrosion; for instance primary sulphur in direct contact with iron will cause a cathodic depolarization with a very high degree of corrosion at a relatively high red-ox potential.

Anything exact of the complexity of soil in relation to corrosion has not been shown, but easily decomposing organic material seems to be stimulating. Therefore the corrosion under heterotrophic conditions is stronger than under autotrophic conditions, which is shown clearly by laboratory experiments. Bivalent iron therefore also stimulates the corrosion, and the content of bivalent iron thus is an important factor. Under autotrophic growth the corrosion seems to be very small when no bivalent iron is present.

Cases also have been reported where all outer conditions for corrosion are present, yet with the iron still not showing any sign of attack. This applies especially to archeological finds of iron objects which very often are very well preserved in soil believed to be active. It has been proved that the lack of corrosion in such cases is due to the fact that the soil contains tannates or is especially rich in phosphates. It is believed that leather articles etc. were buried with the iron objects, and the tannates originate from these articles. Tannate restrains the growth of sulphate-reducing bacteria totally in 0.01 % concentrations whilst 0.001 % concentrations mean a considerable restraint. The phosphate forms complex connections with iron and this complex forms a protecting film around the articles. In such places the phosphates originate from organic materials like food, animals and, frequently, human beings buried with their artifacts.

Lack of corrosion in places where it should be expected in two cases in England has proved to result from the distribution in the soil of Actinomycetes (micro-fungi) which form antibiotica hitherto unknown, and which prove to be very active towards the sulphate-reducing bacteria.

Contrary to the greater part of the papers examined, which support the theory of v. Wolzogen Kühr in explaining the anaerobic corrosion of iron in a neutral soil, are two papers by SPRUIT and WANKLYN (1951). They carried out a comparison of corrosion by heterotrophic and autotrophic growth of the sulphate-reducing bacteria and found that, during autotrophic growth, far more hydrogen is set free than is consumed in reducing sulphate and CO_2; surplus hydrogen is collected in the medium. Further, the authors propose to show that the corrosion in pure autotrophic substrate media has about the same magnitude as in the same media inoculated with sulphate-reducing bacteria. In a later work the same author shows that inoculation by sulphate-reducing bacteria in a pure heterotrophic medium where an iron electrode has been permitted to reach stable value is followed by a drop in potential. This again is followed by a gradual increase of the potential to a higher value than it had originally. In an autotrophic medium, however, the inoculation did not cause any change in the potential value. Further, if to the autotrophic, inoculated medium an organic hydrogen donor is added, a decrease of the potential results. Then the potential gradually increases to a value higher than it had originally. From these tests the authors conclude that v. Wolzogen Kühr's theory that the accelerating effect which the sulphate-reducing bacteria cause in the anaerobic corrosion of iron is due to the cathodic depolarization of the iron because the hydrogen oxidizes, cannot be correct, and that the corrosion must be caused by another bacterial effect, for instance that the sulphide formed acts as an anodic stimulator.

In another paper WORMWELL and FARRER point to the fact that corrosion is strongest where the difference in potential between the pure and the inoculated media is highest. Since the original negative potential does not increase negatively when the corrosion current increases, the authors believe that the activity of the bacteria must act in a depolarizing manner upon the cathode as well as upon the anode.

The articles which I have seen from these last mentioned works are rather brief, and, in my opinion, are no complete basis for an evaluation of v. Wolzogen Kühr's theory.

d. References on anaerobic bacteria and bacterial corrosion.

[after Emmy Egidius Möllerud (1960)]

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CHAPTER V

PREVIOUS VIEWS IN NORWAY AND IN OTHER COUNTRIES ABOUT CORROSION

Since uncovered slender steel piles came into use in Oslo, several views have been expressed about the danger of corrosion. These views have been based partly upon theoretical investigations, partly upon observations from recovered steel objects and beams or piles in the Oslo clays. The material investigated, however, has been limited, and the soil characteristics known, and the number of piles extracted have been insufficient to determine all the factors to-day regarded as necessary for a full understanding of corrosion. Consequently we caannot use the previous material very much.

Among the cases referred to the Oslo Building Authorities are some steel piles from a building site at Filipstad in the Oslo Harbour area, and an iron beam from Halling School in the centre of the city. These piles created a very good impression when they were examined, and, based mainly upon these two examples, slender steel piles without concrete cover were permitted by the Oslo Building Authorities, provided the *p*H-values was above 7,0. If the soils gave an acid reaction, steel piles were not permitted. The pile from Halling School was said to be about 40 years old when it was extracted, whilst the piles from Filipstad were 25 years old. Chemical analysis carried out by professor J. H. L. *Vogt* proved that the clay at Halling School had low salinity. The maximum content of chlorine was 90 mg per 1 000 g of moist clay. In the most saline clays of the Oslo region the salinity may be about a hundred times as high as this.

More recent investigations have been carried out on a piezometer pipe in Parkveien in Oslo. This pipe was put down during the construction of the Holmenkollen subway. The pipe was 11 m long, and had been underground for about 25 years when it was withdrawn. It proved to be pitted and unevenly corroded. The maximum amount of corrosion was about 1,5 mm, with an average loss of 0,15 mm in the deeper parts. Even in this case the clay proved to have an alkaline reaction.

The geotechnical office of the Norwegion State Railways has carried out extensive practical investigations in order to elucidate the corrosive power of the Oslo clays with regard to steel. As early as 1939 Chief Engineer Sverre SKAVEN-HAUG (1956) expressed doubts as to the absolute validity of the *p*H-criterion. He ordered 10 different test piles of accurately measured 20 mm reinforcement steel to be rammed in the clays of South-Eastern Norway, mainly in the city area. Seven of these test piles were placed around the Oslo Ø. railway station, as it was expected to be the site for intensive building activity in the future. Three test piles were placed in the region of Sarpsborg, and subsequently other piles were placed at different localities. In 1939 three piles were placed at Lillestrøm, and in the years 1947–1949 another fifteen piles were driven in the Oslo city area, so that, in all, the material investigated consisted of 28 test piles. In 1947 the first piles were extracted near the Oslo Ø. railway station. All piles had been measured and weighed accurately before placing in the ground. The measurement of the diameter was carried out by micrometer in two directions normal to each other for each metre length of the pile. After extraction, the piles were measured at the same places (Fig. 15). Along with the investigations of the piles, thorough examniation of the soil was carried out. The following factors were determined:

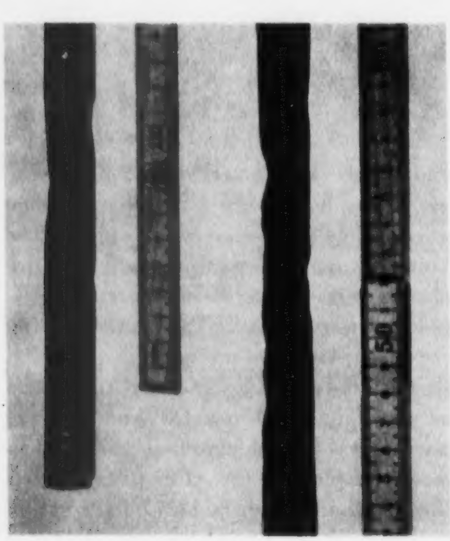

Fig. 15. Corrosion on the test rod, Norwegian State Railway.

The contents of organic material,
The loss by ignition,
The content of carbonates,
The *p*H,
Quantitative and qualitative determination of sulphate.

In some cases the sulphate-reducing bacteria content was determined by Amanuensis Olaug *Sømme*.

The test piles first examined proved that strong variations in corrosive power occur. Some of the piles had been corroded all through during the 10 years' period in the soil. In other cases no measurable attack was found. Thus the amount of corrosion varied between more than 1 mm per year, in the maximum cases, and insignificant values in the minimum cases.

The Norwegian Geotechnical Institute has had opportunity to take part in later examinations, and the co-operating with the laboratory of the Norwegian State Railways has been of the greatest importance for the very complicated problem in corrosion technique. Further material for demonstration was given us by Professor Allan *Bergfelt* of Chalmer Technical University, Gothenburg, when Head of the Construction Bureau of Gothenburg Harbour. In co-operation with the Gothenburg Authories the Norwegian Geotechnical Institute has carried out soil investigations by means of the corrosion probe at the places where piles had been extracted. One place was at the dolphin at Lärje, in the Göta river. This dolphin was rammed in 1929 and extracted in 1955. Its total length was 9 metres. Of these, 4 metres was below sea-bottom level. This dolphin was examined thoroughly along four vertical lines, and showed an average corrosion of about 1,5 mm in the water, and some few tenths of a mm in clay soil, up to an average value of 0,4 mm. This case is dealt with more thoroughly later. As the clay soil in Gothenburg has great similarities with the clays of Oslo, these examinations are very relevant to our programme. The investigation proved that, in the water, pronounced pitting phenomena occur, whilst in the soil there occurs very even corrosion. In this case we have to remember that the part of the steel which was in the water phase, and which had most strongly corroded, to a certain extent may have protected the deeper parts from attack. The pitting factor in the soil was found to be below 2,0, whereas in the water zone pitting factors between 6 and 7 were found. The average annual attack on the worst places in the clay according to the measurements should be of the order of 0,015 mm pr. year. This is less than the permissible values for foundation of buildings.

A 7 m long H-beam pile rammed in 1941 by a quay shed at the Lindholm quay in Gothenburg was extracted. This pile was 14 years old when examined. The upper two metres were covered by concrete. The attack on the pile had been extremely low. On the outer side of the flanges the millscale was still intact. On the rest of the pile the millscale had been attcaked, and some one tenth of a mm of corrosion could be seen. In the same way the millscale was lacking around the welds, but no attack worth mentioning could be noticed. At 8 m depth, pitting with broad pits up to 0,5 mm was found. In this case it could be shown that there were variations in specific resistance and depolarization in the ground.

In Nordenskiöldsgatan in Gothenburg a 25 year old pile, made of two U-steels welded together and the centre-space filled with concrete, was examined. Even in this case the attack was insignificant. The millscale was lost, and a further attack of an average of 0,1 mm was evaluated. In the deeper part, however, broad pits of an area of up to 10 cm^2 with a depth of 0,5 mm were found. Here we had an average attack of the order of 0,005 mm per year, and a maximum attack of 0,025 mm per year. BERGFELT (1957) deals with some other cases, for instance combined steel and wooden piles from A/B Götaverken.

In co-operation with the Swedish State Railways the Norwegian Geotechnical Institute has also carried out investigations at the Uglum Bridge east of Gothenburg. A steel pile which had been in the ground for about 20 years was examined. This pile had not been measured sufficiently accurately before driving, and the values found are subject to some uncertainty. However, it is probable that a loss of 0,25 mm, corresponding to 0,01 mm per year, has taken place.

Further material was not available when this survey was started.

As to the corrosive power of the Oslo clays, however, we have some very instructive reports from earlier times by Professor L. Tronstad and Chemical Engineer Romund Ystad of the Norwegian Technical University at Trondheim. These reports from the late thirties (TRONSTAD, YSTAD, and HAUKELID, 1939) deal with the corrosion of steel piles at Schous Brewery, Oslo. Professor Tronstad's view of the factors influencing the corrosive power was a remarkably modern one. "The acidity may vary from a *p*H of 6 up to *p*H values of 9, and even beyond these limits. In most cases, however, we know that *p*H is not the controlling factor. The conductivity is of far greater importance." Furthermore, Professor Tronstad points to the importance of the transport of oxygen and water to and from the surface of the steel. His conclusion was that the corrosion process was so complicated that he could not recommend the use of H-profiles in an unprotected state in the Oslo region, even in cases where the *p*H -values was above 7,0. He recommended the use of a concrete cover or massive cross sections, and mainly circular piles. As to the possibility of using copper-bearing steels he found that addition of copper to the steel would hardly be of any benefit except where sulphate-reducing bacteria were present. These modern viewpoints were not evaluated to their full extent. Because of the war, Professor Tronstad did not get the opportunity to continue his investigations of the nature of the corrosive power of a soil, and when he fell during the war, there was nobody who could continue his work. This may be the reason why the *p*H-criterion persisted for more than 15 years in the manuals of the Oslo Building Authorities.

In several papers, references to attack upon archeological artifacts have benn used as corrosion criteria. This is dealt with in a later chapter. A great number of investigations on the corrosion of steel and cast iron in soil from areas outside Scandinavia are dealt with by LAQUE (1955) (In: *The corrosion handbook).* Fundamental processes are treated and several investigations are taken into account. From New Zealand, where the conditions in many cases may resemble the Scandinavian ones, references are given also to thorough investigations. G. D. GEMMEL (1952) carried out investigations based on about 100 plates of mild steel, buried from 1934 to 1946 and 1948 in the areas of Oakland, Christchurch, and Wellington, and discussed the correlation between the corrosion and the composition of the soil. The investigations clearly prove that we cannot outline a clear relation between any of the single properties and the corrosive power. However, when the different properties were considered together, certain systematic results came out. From an investigation in the laboratory carried out with a *Denison corrosion cell* good agreement with the actual values was obtained in 75 % of the cases. In 25 % of the cases, however, the field observations and the predictions based upon the laboratory test with the Denison cells gave no positive correlation. Gemmel stated that the most important factor in the furthering of corrosion is to be found in variations in the oxygen content, very low *p*H, high total acidity, good electric conductivity and high capillarity. The factors which may cause the growth and activity of the anaerobe sulphate-reducing bacteria were the same as dealt with in the previous chapter on these bacteria, namely the lack of free oxygen, the presence of neutral salts and organic material, and the presence of sulphate or other oxidized sulphur compounds. Based upon his investigations of the buried plates, Gemmel gave some parameters such as maximal penetration and average attack. The ratio between these two factors is called the pitting factor. In the cases dealt with by Gemmel this pitting factor may vary between 2,3 and 13,9, with a pronounced maximum of about 5. In most cases the average annual corrosion was of the order of 20 microns.

The maximum value for the average corrosion is given as 0,00207 inches, which is a little less than one twentieth of a mm. The minimum value for the average corrosion was as low as 0,00007 inch., or about one twothousandth mm per year. These values seem to be of the same order as the average values found in Norway. However, our maximum attack may be about one twentieth of a mm. A factor which has often been regarded as paramount, and which is also mentioned by Gemmel, namely the total salinity of the soil, does not give an unequivocal criterion. If we plot the values of the corrosivity and the total salinity given by Gemmel, we observe a complete disordered scattering of the points. The diagramme looks like a picture of the stars in the sky. Even the ratio between the specific resistance and the corrosivity does not give any clear relationship, despite the fact that most of the soils where relatively low corrosion has been observed show high resistive values. However, when the different factors are put together, we obtain a somewhat more satisfactory explanation as to why certain soils have high corrosive power, and others have low corrosive power.

The United States National Bureau of Standards has carried out research on underground corrosion for more than 45 years. The results of these investigations have been published in several papers, and different means of protection have been discussed. In 1958 (*"Underground corrosion; a summary of 45 years of research"*) a brief summary of how various metals have corroded in various soils was given. Generally it is seen that cast iron or steel corrode much quicker than copper, lead, or zinc. The conditions, however, are by no means constant, and the relative velocity of corrosion between the different metals, especially copper, lead, and zinc, may be very variable. In some soils it is found that zinc corrodes more quickly than iron, and copper corrodes more quickly than lead. In other soils lead corrodes more quickly than copper. As long as we are dealing with iron and steel alloys there is no clear relationship between the velocity of corrosion and the composition of the metal, if the alloy metals are below certain limits. The same has been found by several other authors.

In a collective paper in the "Iron Age," 1958 (*"Long-range field burial study probes underground corrosion"*), the National Bureau of Standards deals with variations in corrosion as a function of time in various soils. In some soils the attack goes on at nearly constant velocity, whereas in other soils there is a severe attack during the first 1–2 years, but subsequently a much lower velocity of corrosion. The average maximum attack varies between 1 mm per year and one twentieth of a mm pr year. In some soils it seems as if cast iron is attacked mainly by pitting, whilst steel seems to be more evenly attacked. In other soils pitting may be found in all different steel and iron alloys.

Concerning the corrosion of reinforcement steel in concrete several series of experiments have been carried out, but, as far as we can see, only in concrete which has not been buried in normal soils; we have no experience of the standing of reinforcement steel in concrete foundation piles. The general viewpoints dealt with in the earlier chapter, however, seem to indicate that such steel normally will not be attacked by corrosion, even in cases where the concrete piles have minor cracks, provided the content of aggressive carbon-dioxide in the water is low. This is normally the case in our marine clays, where the often considerable content of calcarious organisms and sea shells neutralizes the content of aggressive carbon-dioxide, changing it into bicarbonate ions. In peat layers, and perhaps in gravel seams, aggressive carbon-dioxide, however, may be present, and in cases of damaged concrete piles passing through such layers we have a theoretical chance of serious attack upon the reinforcement steel But, as mentioned, no experiments concerning this have been carried out, and nowhere such attack has been found where piles have been extracted. In cases with aggressive carbon-dioxide, the *p*H-value of the water of course will be fairly low, and the old criterion of the Oslo Building Authorities would be of use. However, this criterion excludes the use of steel piles in so many soils where the aggression is supposed to be negligible and permits it in so many cases where the attack may be serious that we consider the *p*H-determination as unnecessary and unimportant. The Oslo criterion is not based upon the existing scientific facts, but mainly upon philosophical ideas.

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CHAPTER VI

ANTIQUITIES AS CRITERIA OF CORROSIVITY

In two previous papers–1954 and 1955–the present author has pointed to the fact that the majority of the well-preserved Norwegian iron antiquities originate from districts outside the sea area which was covered by sea water during and after the last Ice Age. In the marine clay areas in eastern Norway iron objects normally are severely corroded, and most often only lumps of rust are left. The corrosivity (corrosive power) of the Oslo marine clays obviously is much greater than that of the rest of the country. Reference is made to T. Dannevig HAUGE's investigations (1946). He examined 79 iron objects from pre-historic time in order to determine the melting point. Only one of these objects was found below the "marine limit"; all the other 78 objects originated from areas above this limit, in eastern Norway. This does not mean that all iron antiquities below the marine limit are lost. However, it means that only one object had undergone corrosion so insignificant that Dannevig Hauge thought it reasonable to undertake investigations concerning the original composition of the iron.

In Sweden, O. ARRHENIUS (1956) drew attention to the same phenomenon, namely that corrosivity is much higher below the marine limit than above it.

When the degree of corrosivity of different soils is examined, it must be borne in mind that clays are mostly present below the marine limit, whereas soils such as peat, muck, sands, and other sediments mostly are formed under lacustrine conditions, where the salinity is very low. In the high moor peats the amount of dissolved electrolytes will be much lower still. However, these soils may be present below the marine limit, and they do not vary in their corrosivity from comparable soils above the limit. Therefore it is not sufficient to state that an object is found below the marine limit, it is necessary to investigate whether or not it has been buried in a marine deposit. As the marine deposits are never found above the marine limit, such conditions obviously can be excluded entirely there, whereas below the limit there is a fair probability that the soil is of non-marine origin. Thus it is necessary to undertake more thorough investigations, and not only those based upon the degree of preservation of antiquities, before anything is stated generally as to the corrosivity of a district.

Many other factors add to the conductivity, which is a function of the origin of the soil, whether the soils are deposited in fresh water, salt water, or formed by in situ weathering.

Among the most important inorganic factors are the cathodic depolarization, based upon oxidation, and the content of trivalent iron or tetravalent manganese. The acidity of the soil and the *p*H-value of the moisture are also of certain importance. All these complicating factors make a simple statement about the general corrosivity of a district more or less invalid.

The most important factor to be considered when a pre-historic object is analysed as an idicator of corrosivity is the nature of the other objects which have been buried together with the iron. For hoards and votive deposits it may be supposed perhaps that only metal objects were deposited, even though metallic contacts between iron and noble metals such as bronze, silver, or gold will induce corrosive actions; such deposits easily may be analysed. For funerals, however, there are far more complicated factors. It is well known that phosphates and tannates act as corrosion inhibitors. This has been dealt with by, for instance, T. W. FARRER, L. BIEK, and F. WORMWELL (1953), and by T. W. FARRER (1955). These investigations clearly proved that tanned leather in shoes and scabbards acts as an effective inhibitor, especially when the corrosion is due to sulphate-reducing bacteria. Although it seems as if such bacteria in Norway are not of the same importance as in more southern countries, the upper part of the soil during summer may arrive at temperatures which allow these bacteria to attack steels most severely.

Another important factor which inhibits corrosion of antiquities in Norway is due to phosphate. We investigated several prehistoric objects and found that they were covered by a mixture of trivalent iron phosphate, $FePO_4 2H_2O$, and bivalent iron phosphate-hydrate "vivianite," $Fe_3(PO_4)_2 8H_2O$. For instance, the Oseberg-ship burial is a good example of well-preserved iron nails which have lasted for more than a thousand years in the south-eastern marine clay ground. These nails are so beautifully preserved that we even can see the marks from the hammering when the nails were driven into the ship's planks. The iron does not seem to be either specially pure or safe against rusting in any other way, but in the ship several horses, dogs and other animals, together with food, textiles, and leatherware were buried, as well as the two female bodies. All this organic material, most of it rich in phosphate, had preserved the iron to an astonishing degree.

Arrhenius (1956) discusses the archeological material based upon iron objects from thousands of graves and dwelling places. There is a marked correlation between corrosivity and precipitation in a district and the conductivity of the soil. However, all these objects were found in relatively shallow graves, where the attack of the atmosphere and oxygen-bearing rain water is rather important. The conditions deeper underground are entirely different, and there is no reason to regard the grave deposits as a sufficient indicator of what is going to happen to steel piles.

As mentioned, it is mainly British researh workers who have raised doubts concerning the validity of antiquities as indicators of corrosion. However, it is striking how much stronger have been attacks by the marine clays in south-eastern Norway than by the soils inland, so that it must be inferred that even the corrosion-inhibiting factors which have existed in the graves have not been sufficient to protect the iron in the lowlands, whereas they may have done so inland. It must be remembered that just the same districts of Norway which are to-day's most important industrial areas, in prehistoric time had the most dense and well-to-do population, so that most probably the number of artifacts buried in these districts would have been much higher than in the rest of the country. Therefore, if we look statistically upon the material, the archeological objects give us a certain valuable elucidation of the general corrosivity. The material by O. Arrhenius is convincing in this respect, and, as Arrhenius uses his material to predict the corrosivity of shallow foundations, electric power masts etc., most probably there will be a general agreement. However, we have to be careful if a single, localized site is under discussion. Where a whole district with hundreds and thousands of mast foundations far apart is dealt with, conditions are different.

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CHAPTER VII

THE CATHODIC REACTIONS

Investigations of antiquities and of test piles which have been rammed in various Norwegian soils and later extracted indicate that the corrosion and the corrosivity conditions may vary considerably. Locally, velocities of corrosion corresponding to an attack of more than one mm per year have been found; in other places the corrosion has been minimal. Thus we know of swords from the Roman Age and from the Migration Period which prove that the average corrosivity has caused an attack of the order of only one millionth of a mm per year (Fig. 16). These 1 500–2 000 years old swords may be practically undamaged in some places, and marks left during the grinding of the edges are still clearly visible. All reservations which may be made because of tanning agents and phosphates do not invalidate this extraordinarily low corrosivity. As the tanning agents mainly counteract the activities of bacteria, it is still true that the cathodic inorganic processes, under certain circumstances, may be very slow. Unfortunately we do not know to a sufficient degree the chemical and electrochemical conditions under which these swords have been preserved. We have no determinations of the oxygen content of the pore water or of variations in the chemical composition of the soil along all parts of the swords. In one case which was investigated by the author, namley a Roman sword from Illerup Moor in Jutland, Denmark, the sword was found in consolidated muck, and it seems as if the conditions had been strongly reducing all along

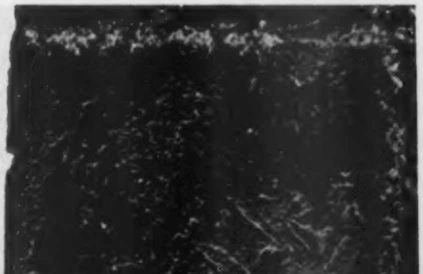

Fig. 16. Sword edge from Hillerup Moor, Denmark. Migration Age. Scale 1.7:1.

the sword. This sword was in a perfect state. In several places the edge was so sharp that it was still possible to cut a finger upon it. The sword was from the Migration Age, about 300–400 A.D. Other cases of intensified corrosion are known with a maximum on piles or pipes which pass through a muck layer, the soil on one or both sides having a low content of organic material. From chemical analysis of the pore water in several series of clays it is found that, below the weathered crust, the pore water is mainly free of dissolved oxygen. Nevertheless, steel piles may be heavily corroded even in such soil profiles. This may be compared with the information of Allan Bergfelt (see page 38) concerning piles at Götaverken A/B, Gothenburg.

Such conditions make it clear that the corrosion processes in normal soil do not depend upon a simple reaction between oxygen-bearing ground water and electrons on the cathodic parts of the piles. Other factors obviously are involved in the process.

For all steel piles which were extracted and investigated at the Norwegian Geotechnical Institute it was found that considerable areas of the pile surface had been covered by a grey, solid layer, which resembled cement, whereas smaller parts of the piles had no such layer. Without exception the attack was minimal to moderate on the areas where the grey cover was found, whereas the attack was moderate to strong on the parts where no such cover was found. Analysis of this grey cover proved that it was characterized by a very great content of ferreous carbonate which acted as an effective mortar holding the clay minerals together. The thickness of the grey cover varied between some tenths of a mm and a few mm. Further, it was found that even the clays at a somewhat greater distance from the steel surface contained $FeCO_3$, the content of which, however, had been insufficient to cement the clay particles together. It seems as if these precipitants of carbonates are formed on the parts of the steel constructions which behave cathodically during the corrosion process, whereas no such cover is formed on the anodic parts. For the sake of simplicity we have normally designated this cover as "cathodic cover."

In one case we drew a test pile together with the surrounding soil, which was cut out as a thick cylinder by means of special boring equipment. The pile, which had been left in the clay for about 10 years, had a continuous solid cathodic cover on most of the surface, and the surrounding clay for a distance of several mm had a "bleached" colour, markedly different from the normal bluish colour of the clay. The nature of this bluish colouration has not been clarified completely, but it seems to be due to finely distributed ferrous sulphide in very minute amounts. In the cathodic reaction this colouring agent must have reacted in some way, which is difficult to explain, however, as the *p*H value obviously increased although diffusion of carbonate or bicarbonate ions towards the cathodic parts took place. However, we have not found it necessary to investigate this point, although the problem obviously is left in an unsatisfactory way.

The cathodic cover seems to have been observed and treated for the first time by the Geotechnical Bureau of the Norwegian State Railways. The head of this Institute, Chief Engineer Sverre Skaven-Haug (1956), has dealt with some test piles in an internal report. In this case some 8 m long piles, of 20 mm cross section carbon steel with an ultimate strength, $\sigma_f = 37$ kg/mm^2, driven in 1938, were examined. In a report from the chemical laboratory of the State Railways an analysis of the grey cover is given. The analysis gives the following values (table 2, see also p. 37):

TABLE 2.

Moisture	1,07 %	
Loss by Ignition	14,91 %	(mainly CO_2)
SiO_2	36,30 %	
Fe_2O_3	31,43 %	
$Al_2O_3 + TiO_2$	5,23 %	
CaO	4,60 %	
MgO	1,38 %	
Chlorides	0,01 %	
$Na_2O + K_2O$ (difference)	5,07 %	
	100,00 %	

(0,01 % chlorides correspond to 200 mg Cl pr dm^3 of cover. Thus the cover is practically free of the marine chlorides.)

The conclusion reached by the chemical laboratory was:

"The composition indicates a clay substance welded by carbonates. However, the content of iron oxides is so high that it indicates a corrosional attack on the steel."

Various subsequent analyses carried out by the Norwegian Geotechnical Institute gave much higher values of $FeCO_3$. X-ray investigations by the powder method gave siderite as the only marked crystalline phase.

In some cases, especially at the Central Railway Station in Oslo, some test piles proved to be severely attacked locally. Some of the steel rods were cut through entirely as a result of corrosion, whereas others had suffered great attacks at narrow localities. However, the greater part of the pile surfaces had suffered no, or insignificant attack. These areas, in all cases, were those which were covered by the light grey ferreous carbonate layer. This finding indicates that the grey "cement" was precipitated upon areas which originally were the cathodic parts, and that these cathodic areas continued as cathodes more or less unchanged througout the time when the piles were left in the ground. Because of this, the areal ratio and distribution between cathode and anode must have been constant, and the attack localized to those areas which for some reason or other started as anodes. The anodic depolarization never became so important as to shift over from anode to cathode. This is a very unfavourable condition, as the anodic areas under certain circumstances may form continuous zones all around some piles and thus make it possible to cut the piles right through on a limited area, although the total loss of iron from the pile may be fairly low. As the cathodic areas under all circumstances seem to be large compared with the anodic areas, even slow cathodic depolarization processes may cause relatively rapid attacks on the anodic parts. Therefore it seems to be of the greatest importance for evaluation of the danger of corrosion to know how the cathodic process takes place. This is especially important for continuous steel constructions, as for instance a net of pipelines in soils.

The very slow corrosion processes which have been found in some cases, for instance where the corrosion has been one millionth of a mm per year, seem to take place under homogenous reducing conditions, especially for small objects the size of an arrow-head or a sword, whereas more extended objects such as piles, pipelines etc., as far as is known, never exhibit such minimal attacks. Thus we have to conclude that if no

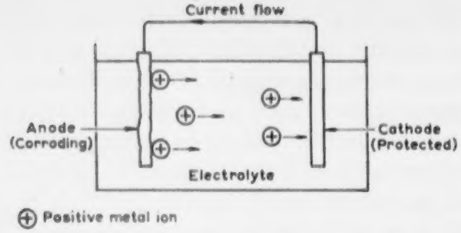

Fig. 17. Schematic presentation of anodic and cathodic areas.

depolarization takes place on the cathodic areas, corrosion of steel in soil will be effectively inhibited. The formation of the cement-like ferreous carbonate cover at the cathodes proves on the other hand that the cathodic part of the depolarization mainly takes place by the consumption of electrons and a simultaneous formation of OH^- ions (Fig. 17). Bacterial corrosion which involves a reduction of sulphates to sulphides does not take place to any greater extent under such conditions, although sulphate-reducing bacteria are known to be present in the actual soils. However, the cement-like cover does not tell anything about how the OH^--ions are formed, whether it is due to a reaction between electrons, water and some oxidizing agent, or to the liberation of H_2 from the H^+ ions of the water phase. Either of these reaction types, of course, will shift the *p*H towards higher values.

As mentioned, it has been found that free oxygen is either absent or present only in small amounts in most subsoils. In other cases the oxygen content may be higher. This is especially the case in the upper strata and in gravel seams. If the content of free oxygen in the ground water is to be determined, the sampling and the treament of the samples must be carried out with the greatest precautions in order to avoid any contamination by atmospheric oxygen. It seems as if the best way to perform such an analysis is on the basis of samples taken with some type of piston sampler. For such samples there are possibilities of undertaking chemical analysis.

The soil samples are pressed from the sampling cylinders into a bowl filled with toluene in order to avoid admission of atmospheric oxygen. From the internal parts of the larger samples, smaller test samples may be cut out by means of a small borer. The clay, of a weight between 2 and 5 g, is brought into a closed distillation apparatus below a layer of toluene. Here it is disperged in 50 ml boiled distilled water. Subsequently 2.5 ml of 10 % $MnCl_2$ solution and 5 ml of a solution containing 4 % of KI and 2 % of NaOH is added. Under these alkaline conditions eventual free oxygen will oxidize bivalent manganese hydroxide to tri- or tetravalent. After a couple of minutes 10 ml. of 10 % boiled solution of citric acid is added. If tri- or tetravalent manganese hydroxide is present, i.e. if any free oxygen was present in the sample, equivalent amounts of I_2 are liberated. This gives a red colour to the toluene layer. The intensity of the colour may be compared to standard I_2 solutions in toluene. Such a comparison is fairly inaccurate. but it is not possible to distil the solution, as any iron sulphide which may be present in the soil will react with the citric acid when hot, liberating hydrogen sulphide, which will reduce the I_2 to I^- ions. After examination of the I_2 content in the cold toluene layer, the sample is heated until all H_2S is liberated and driven off. Subsequently 10 ml. of 20 % hydrochloric acid is added. By this addition, higher oxides of iron and manganese will react with the KI and liberate equivalent amounts of I_2, which may be distilled off together with the toluene. If necessary, additional toluene is added to the distillation flask until clear, uncoloured toluene is coming off.

NB! All reagents which are used for this analysis must be freshly boiled before use. As a control, a blind test has to be undertaken for all reagents.

At a building site in Sandefjord we have carried out various investigations of the corrosivity. A series of analyses gave the following results (table 3):

TABLE 3.

Depth	Free Oxygen	Additional oxidizing capacity recalculated as mg oxygen per g moist clay	*p*H of clay suspension	Ions in pore water recalculated as per cent NaCl
3,70	Not present	0,002	7,76	2,10
4,50	Traces	0,01	7,76	1,89
5,60	Traces	0,01	8,14	2,94
6,50	Slight traces	0,19	8,40	2,26
8,50	Somewhat more	0,84	8,29	2,72
9,60	Not present	0,58	8,43	2,48
10,60	Traces	0,62	8,59	2,58
13,30	Not present	0,14	8,42	2,48
16,10	Not present	0,55	8,33	2,42
18,90	Not present	0,68	8,42	2,22
22,20	Traces	0,54	8,48	2,10
26,00	Very slight traces	0.18	8,52	1,54
29,30	Not present	0,196	8,45	1,26
32,40	Not present	0,41	8,41	1,23
35,70	Not present	0,39	8,40	0,87

As it will be seen later (p. 68) there is no good correlation between the chemical findings in the various strata and the electrical measurements which were performed. Furthermore, there was no good relation with the actual corrosion conditions found on the foundation piles which had been left in the ground for 11 years. We have to conclude that even the mineral phase is of the greatest importance for the corrosion conditions. Several series of laboratory investigations carried out at the Norwegian Geotechnical Institute point in the same direction.

As part of the studies of the cathodic depolarization processes we have tried to simulate the natural conditions, potential-current diagrams having been produced for steel cathodes in media corresponding to those present in natural soils. The steel used was an ordinary mild carbon steel corresponding to the most common pile material. The polarization curves for the steel electrodes were taken against a copper/copper-sulphate half cell as a reference electrode. The potential was measured by means of a Cambridge voltmeter with internal resistance 208 000 ohm and 50 000 ohm respectively. For accurate measurements compensation by means of a dry cell battery was employed. Thus the instrument was used as a zero-current instrument. The salt water bridge between the cell and the standard cell had the same salinity as the aqueous phase in the test container. The polarization curves were obtained for various current densities from a potentiometer coupled to a 2-volt accumulator using a steel help anode. The salinity in the corrosive medium was kept constant at 3 g sodium chloride per litre water. The following media were examined:

1. Salt water free from oxygen under a layer of toluene.
2. Salt water with oxygen bubbling through.
3. Salt water in which freshly precipitated trivalent iron hydroxide is suspended. No oxygen admitted. *p*H 7.

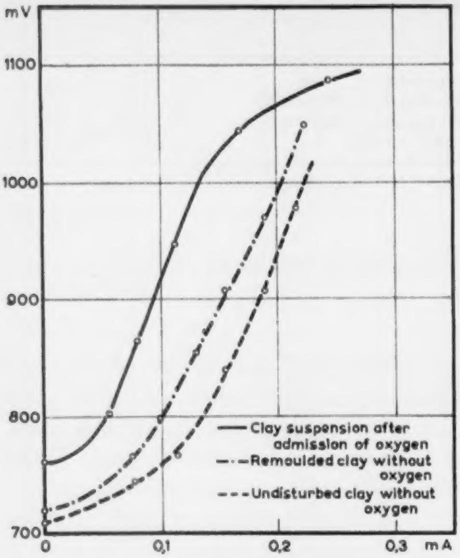

Fig. 18. Effect of oxygen as depolarizer.

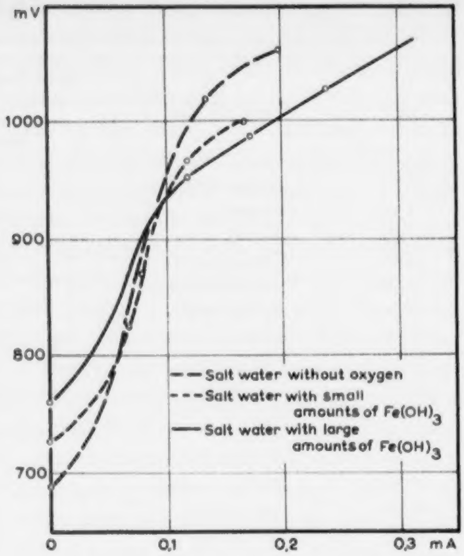

Fig. 19. Effect of oxygen and $Fe(OH)_3$ as depolarizer.

4. A suspension of hydrous mica clay from Southeastern Norway, suspended in salt water without admission of oxygen.
5. The same as series 4, but oxygen bubbling through.
6. Similar to series 4, but in this case with a hydrous mica clay which in advance had adsorbed trivalent iron. In this suspension the *p*H was adjusted to 7 by means of ammonia. Thus the concentration of dissolved trivalent iron in the solution is comparable to the solution in a suspension of trivalent iron hydroxide series 3.

The conclusion drawn from the experiment is that bubbling of free oxygen through a suspension acts as an effective depolarizer, whereas the addition of a clay suspension is of minor influence. However, as a clay where trivalent iron is adsorbed in exchangeable position acts as a very effective depolarizer, it seems that the trivalent iron adsorbed upon the mineral surface has a great ability to take up electrons, changing to bivalent. At the same time the free valencies are neutralized by hydronium ions. There is obviously a marked difference between trivalent iron which is adsorbed upon the clay mineral surface and the trivalent iron which is present in the state of hydroxide. Even for a freshly precipitated hydroxide, the iron is present in a crystalline structure, and even though such an hydroxide may contain a high number of defects and dislocations, the reaction of trivalent iron is very much less than the reactivity of the adsorbed trivalent iron in exchangeable positions in an ion-exchanging substance.

The results of the measurements are seen from Figs. 18, 19, 20, and 21.

All readings were taken at temperatures between 23 and 24° C.

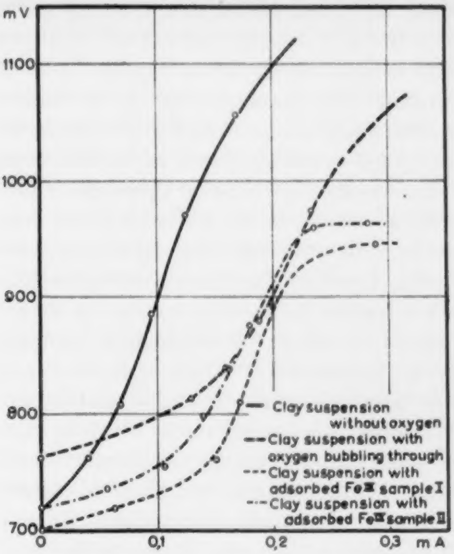

Fig. 20. Effect of oxygen and adsorbed trivalent iron as depolarizer.

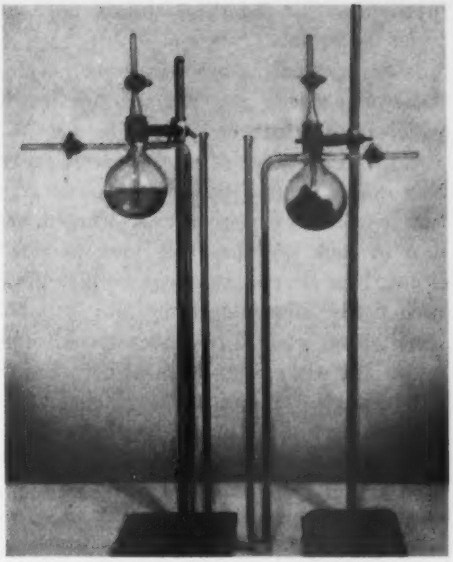

Fig. 21. Reaction between gaseous hydrogen and clay in the Fe^{+++} state.

In order to examine this further we have carried out some tests concerning the reaction between gaseous hydrogen and trivalent iron ions at room temperature. Two congruent glass flasks were fitted with a mercury manometer. In the one flask was placed a solution of trivalent iron sulphate, in the other a moist clay which had adsorbed the same quantity of trivalent iron. The flasks were filled with hydrogen at atmospheric pressure, and sealed off. The pressure in the flasks could be observed by means of the mercury manometer (Fig. 21). The experiment proved that the pressure steadily decreased in the flask where the iron was adsorbed upon the clay minerals, whereas no noticeable change in pressure took place in the flask where the iron was dissolved, although the iron concentration in the liquid phase was very much higher in this case than in the case of the clay. In order to make certain that the consumption of hydrogen in the case of the clay was not due to bacterial activities, the clay was made acid by means of hydrochlorid acid. When the experiment was finished, no hydrogen sulphide could be smelt; it seems as if the action of sulphate-reducing bacteria may be excluded.

From this and other experiments, we infer that the clay mineral may act as an effective catalysts for the reaction between trivalent iron ions and gaseous hydrogen under formation of bivalent iron ions and hydronium ions.

This catalytic effect of the clay mineral upon the reduction of hydrogen seems to be of fundamental importance for the understanding of the corrosion process. We have a certain analogy in the well-known fact that a solution of trivalent iron ions is easily reduced to bivalent when gaseous hydrogen is bubbled through it, provided platinated platinum is present, but not if platinum is not present. The mechanism in this case seems to be that the platinum dissolves hydrogen which reacts from the "metallic state." The mechanism for the clay mineral most probably is different, although the effect seems to be the same.

For cathodic depolarization, therefore, it seems as if an electron transfer between the iron cathode and the surrounding medium may take place through a mechanism which invites further study. The transfer may take place across considerable distances, at least of an order of magnitude of several mm, which again represents more than 1 000 clay mineral particles. This catalytic effect caused by the clay mineral upon the reduction/oxidation process seems to be connected with variations in the activities of the iron ions in such systems. This may be due to the fact that the adsorbed ions partly are situated in an electric field in the diffused double layer of the minerals. The cation-exchanging minerals of the clay group are characterized by a sheet lattice. In montmorillonites and illites there are alternating layers of silicon in tetrahedron configuration and aluminium in octahedron configuration, the corners of which may be oxygen or hydroxyle. To a certain extent the silicon in the tetrahedrons is replaced by aluminium, and the aluminium in the octahedron may be exchanged for manganese or bivalent iron. Thus we arrive at an excess of negative charges which may be as high as 150 equivalents for 100 g of minerals. This excess of negative charges is compensated by adsorbed cations on the surface or between the sheets. The distribution of the adsorbed cations depends upon the concentration in the liquid phase and the polarizability and charge of the ions. It may be illustrated as Figs. 22 and 23. Under such conditions the electrochemical potential μ_i is given by the sum of the chemical potential $\mu + R\,T \ln a$ and the electrical potential $2F\psi$.

$$\mu_i = \mu_i^\circ + R\,T \ln a + z_i F \psi$$

where

μ_i° is standard chemical potential for the ion
T is absolute temperature
R is universal gas constant
a is ion activity
z is the valency of the ion
F is the electric charge of a gram-equivalent
ψ is electric potential for each charge unity and valency at the position of the ion against a reference level.

We have the ratio between the ionic activity in the adsorbed layer and in the standard solution:

$$a_a / a_o = e^{zF(\psi_o - \psi_a)/RT}$$

For the cations in the vicinity of an electro-negative surface the electric potential is negative, and consequently the activity will be high. This factor is discussed by J. V. Lagerwerff (1958) in connection with the adsorbtion of fertilizers in soil. It seems as if the adsorbed iron ions on the clay mineral surface have an increased activity as a result of this factor. At the same time, however, we have to assume that even the H^+ ions which are formed at the reaction will have an increased activity, whereas eventual neutral H atoms or H_2 molecules will be polarized in the electric field surrounding the minerals. This polarization will be caused partly by the negative charge of the minerals themselves, and partly by the high concentration of cations in the double layer. No exact measurements have been carried out concerning the heat of reaction when neutral hydrogen is diffusing into the double layer and reacting with the adsorbed trivalent iron. However, there is no reason to assume that this heat of reaction will be markedly higher than the heat of reaction in the non-adsorbed non-condensed systems. *We have to assume therefore that the energy of activation for the reaction between hydrogen and adsorbed iron will be depressed from the value represented by the corresponding reaction in the non-adsorbed system.*

Our working hypothesis consequently is the assumption of an electron transfer between the iron cathode and trivalent iron adsorbed on an ion-exchanging substance at a certain distance from the electrode, caused by diffusion of an intermediate neutral hydrogen atom or molecule which is dissolved in the liquid phase at a pressure insufficient for the formation of bubbles. The reactions assumed consequently are expressed in the following manner:

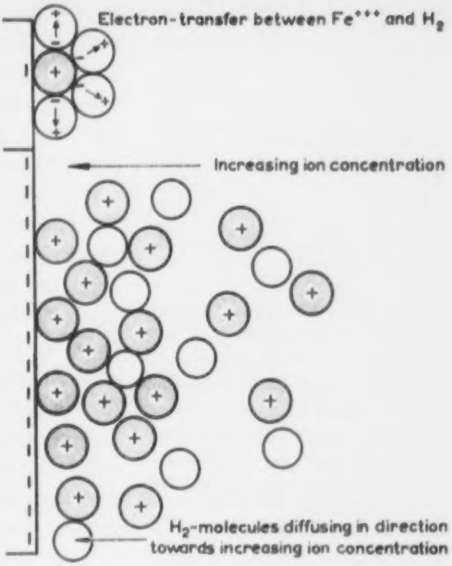
Electron-transfer between Fe+++ and H2
Increasing ion concentration
H2-molecules diffusing in direction towards increasing ion concentration

Fig. 22. Schematic presentation of the electron transfer between tri-valent iron and an iron cathode by an intermediate reduction oxidation process in hydrogen.

$$2\ \text{Clay Fe}^{+++} + H_2 \rightarrow 2\ \text{Clay Fe}^{++} + 2H^{+}$$
$$2H^{+} + 2e^{-} \rightarrow H_2$$

The effect of an ion-exchanging substance in the ferric state upon the depolarization of an iron cathode is elucidated by the following experiment:

Four congruent plates of mild steel, each having a surface area of 10 cm^2, were placed in four reagent tubes in a solution bearing 1,33 Molar respectively to KCL. In two of the four tubes, an iron-exchanging resin, Zeo-Karb 225, The Permutite Company Ltd., was placed below, but not in contact with, the steel plates. The ion-exchanging resin was treated with Fe^{+++}, and subseqpently rinsed with distilled water until there was no positive reaction with KCNS. In the two other reagent tubes there was no resin; otherwise the steel plates were placed in the same position as in the first-mentioned case. In each of the two series, half of the surface of one plate was coppered, whereas the other half was left bright.

After 70 days an explosion took place in the tube containing the non-coppered plate and the resin. The plate had suffered a loss of 14,1 mg. Because of the explosion it was not possible to collect all the resin. However, roughly one half of it was collected and investigated. This part was found to contain 41,3 mg Fe^{+++} and 6,1 Fe^{++}.

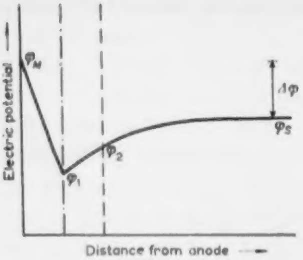

Fig. 23. Schematic presentation of the variation in potential in the electrochemical double layer at the border face anode/electrolyte solution. (Some of the ions from the solution are specifically adsorbed to the surface of the electrode.)

After 169 days the other tube containing resin exploded. The greater part of the resin was collected. Originally this had contained 103 mg Fe^{+++}, 0 mg Fe^{++}. On investigation the resin was found to contain 72 mg Fe^{+++} and 100,4 mg Fe^{++}. The loss in weight of the steel plate was 120,4 mg.

Considering the time of corrosion, it is obvious that the velocity of corrosion had been much higher in the case of the copper-plated piece than in the case of the non-coppered steel. Further, it was demonstrated that, although the distance between the steel plate and the ion-exchanging resin was several cm, the trivalent iron in the resin to a great extent was reduced to bivalent. Obviously 31 out of the 100,4 mg of bivalent iron originated through the reduction process, whereas the rest corresponded to iron ions liberated by the corrosion process. Moreover it was demonstrated clearly that the amount of hydrogen which caused the tubes to explode bore no relation to the loss in weight caused by the corrosion of the steel. Consequently, the mechanism of corrosion was not a simple liberation of hydrogen.

The two other tubes were opened when the last tube containing ion-exchanging resin exploded. The loss in weight of the non-coppered plate was 1,4 mg, and that of the coppered plate 8,0 mg. The catalytic effect of the resin thus seems to be obvious.

As the cathodic processes control the velocity of corrosion of steel in the *p*H-range 5 to 8, it must be assumed that the electron transfer is caused by ionic transport and diffusion.

Even though the concentration of Fe^{+++} is low, it may be assumed perhaps that Fe^{++}, which is liberated at the anodes, will diffuse to the ion-exchanging resin and replace Fe^{+++}, which may diffuse to the cathode, and depolarize it by taking up an electron. In order to investigate this point, we have carried out experiments with a circulating liquid system and an iron electrode which was given the potential of – 600 mV E_h by means of a graphite help anode. The liquid phase was made to circulate, passing the iron electrode above the clay in the Fe^{+++} state. At the beginning of the experiment the *p*H was 7,3; at the end of the experiment the corresponding value was 7,58. At the same time, 1,17 % of the trivalent iron was reduced to the bivalent state. The increase in the *p*H-value is assumed to be due to adsorption of H^+ in order to keep up the electron neutrality by the transfer from

$$\text{Clay } Fe^{+++} \rightarrow \text{Clay } Fe^{++} \cdot H^{+}$$

Obviously a diffusion of trivalent iron from the clay to the electrode is impossible in the circulating system, thus proving that another mechanism, and most probably the suggested one, takes place.

CHAPTER VIII

THE CORROSION PROBE

As the natural corrosion processes which may be expected on steel piles are considered to be purely electrical in nature, the Norwegian Geotechnical Institute has developed a probe, with the object of registering the magnitude of some of the factors which are considered important in the electro-chemical corrosion processes. The probe consists of a 0,5 m long steel pile with a magnesium point which is insulated electrically from the pipe. When the probe is driven into the ground and the two metals are connected electrically, they form a corrosion cell. If an ammeter is connected to the circuit, it is possible to measure the current flowing between the two metals, and with a resistance bridge the pure resistance between the poles can be determined. This bridge operates on an alternating current with a frequency of 600 cycles/second, thereby preventing polarization of the poles. When the probe is short-circuited, the cathode and the anode become polarized, and a reverse voltage is developed at the surface in contact with the electrolyte. The difference between the electromotive force in the unpolarized state and the reverse voltage represents the operating voltage of the corrosion cell during the corrosion process. This voltage is obtained from the measured values as a product of the resistance of the cell, which is the resistance through the soil, and the current which flows when the cell is short-circuited. The effect of resistance in the cable of the instrument is so small that it can be neglected in the calculation. We thus can state:

$$E_P = E_u + E_{kp} + E_{Ap}$$

Where:

E_P = cell's electromotive force in a polarized state.
E_u = cell's electromotive force in an unpolarized state.
E_{kp} = polarization voltage at the cathode.
E_{Ap} = polarization voltage at the anode.

$$\text{and } E_P = R_j \cdot I_P.$$

where R_j = pure resistance between the poles in the soil.
I_P = current obtained when the cell is shortcircuited.

By placing the cell in a saline solution of diluted H_2O_2 one can consider that the polarization will be a minimum; the electromotive force measured can then be expressed as follows:

$$N = E_p / E_{uo}$$

where

E_{uo} = the electromotive force in the reference medium.

N = the ratio between the electromotive force in the tested material and the reference medium.

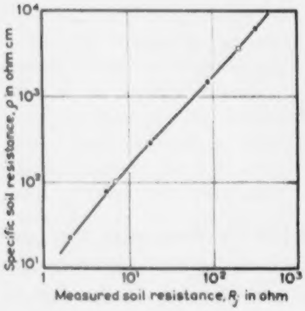

Fig. 24. Specific soil resistance (ρ) as a function of soil resistance (R_j) measured with the Norwegian Geotechnical Institute's corrosion probe.

The values of E_u vary only slightly with surrounding material, therefore, the ratio N is mainly dependent upon the polarization and is known as the depolarization coefficient (the numeral value of N increases with decreasing polarization).

On the basic of the measured values for the soil's resistance the specific resistance can be derived from a calibration curve which relates these two values. (Their mutual relationship is, however, a very complicated function.) See Fig. 24.

When the values for depolarization and specific soil resistance are obtained, two of the factors that determine the corrosion rate are thereby known. A third factor, potential differences caused by inhomogeneities in the soil's electrolyte, does not lend itself to direct observation. As is the case with the potential differences at the outer surface of the steel, it is also the potentials in the electrolyte that effect the corrosion rate. These certainly influence the values for E_P, but the effect is completely overshadowed by the other factors.

The values determined with the probe express the tendency for corrosion but no absolute value of the corrosion rate can be derived from them. To be able to make use of the measured values it is necessary to find from experience the corrosion rate in different media. For example refer to table 4.

From this table we have the possibility of calculating an average value for corrosion in the ground based upon the empirical data found from the test piles. As clearly shown, however, this average value may be modified by geological factors, such as the gradient of the pore-water pressure, the natural slope etc. Further the corrosion will be concentrated upon particular parts of the piles if inhomogeneities exist in the soil's electrolyte or temperature, which is normally the case. Accordingly we have proposed the following relationship between the corrosion groups mentioned earlier, the specific soil resistance and the electromotive force of the cell in a polarized state:

Corrosivity group 1	Unmeasureable corrosivity.
Corrosivity group 2	Harmless corrosivity.
Corrosivity group 3	Corrosivity which under unfavourable conditions may harm slender pile constructions.
Corrosivity group 4	Corrosivity which normally will harm steel piles.
Corrosivity group 5	Very high corrosivity. Steel piles not to be recommended.

TABLE 4

Table showing the relationship between corrosivity group and electrical data.

Cell's MF in % of max. value	< 40 %	40–60 %	60–80 %	80–100 %
specific soil resistance < 100 ohm cm	2	3	4	5
specific soil resistance 100– 500 ohm cm	2	3	3–4	4–5
specific soil resistance 500– 2 500 ohm cm	2	2	3	4
specific soil resistance 2 500–12 500 ohm cm	1	2	2–3	3–4
specific soil resistance > 12 500 ohm cm	1	1	1–2	2–3

An average corrosion of the order of 0,02 mm per year is considered to constitute a harmful corrosion. With normal piles and loads this will bring failure within 150 years, provided that the attack is even.

This relationship can be put up in a continuous scheme as seen from Fig. 25, where the corrosion rate is given as a function of the degree of depolarization (n) and specific soil resistance (p) for homogeneous Norwegian clay.

The values for salinity and depolarizing power which may be obtained by means of the corrosion probe can also be determined by analysis of samples. Such analysis is relatively complicated, and a careful treatment of the samples is necessary. With the corrosion probe it is possible to take the borings and measurements at a speed of 3–4 min. per metre depth at least down to 40 m.

In the above approach to corrosion only homogeneous corrosion is dealt with, i.e. the all-over corrosion obtaining for homogeneous steel in homogeneous soil. The influence of chemical or biological variations which may take place after the pile has been driven into the soil has not been taken into account. It would be of help to have some general physical equation by which the results may be compared, and we have found that an equation of the following type is valid:

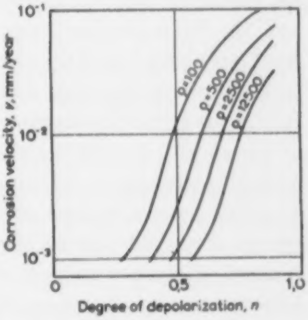

Fig. 25. Corrosion velocity (v) by homogeneous conditions as a function of the degree of depolarization (n) and specific soil resistance (ϱ) for Norwegian clay.

$$K = (kE/\ln R) \cdot f(dE/dx) \cdot f(dR/dx) \cdot f(dT/dt) \cdot f(T) \cdot f(q)$$

where:

E = effective elctromotive force in per cent of the max. value of the probe.
R = specific soil resistance.
T = temperature.
t = time.
q = product of permeabiliy and hydraulic water pressure gradient.
x = longitudinal extension of the construction.

Obviously the equation given above is not to be taken literally, as we do not know the various parameters. However, from example given earlier it is evident that the variation in resistance and depolarizing capacity along the extension of the metal object (pile or pipe line) is of paramount importance for the localising of the attacks. The influence of the temperature itself may be very high, especially in cases where bacterial corrosion is active. The probe itself registers the activity of bacteria in the present soil, and in many cases we have found high values for the effective electromotive force in the polarized state, obviously due to bacterial activity. When such a soil acquires a higher temperature after the building has been placed upon it, even higher values for depolarization may be expected. For instance, the soil temperature in south-eastern Norway is 6–8° C as an average. Under extended buildings the ground temperature will rise steadily up to 20 ° C or even more.

The theory of the corrosion probe.

The electro-chemical processes which take place when steel piles or other steel structures corrode in the soil are controlled chiefly by the degree of polarization. If it had not been for the polarization phenomena (including the hydrogen overvoltage on steel) we should hardly find any soil of such low corrosivity that steel piles could be used in it. In a homogeneous soil the anodic and cathodic areas arise on various places of the steel pile, depending upon inhomogeneities in the steel, mechanical stresses or orientation of the grains, or the presence of millscale etc. With a completely homogeneous steel in a non-homogeneous soil we will obtain in the same way cathodic and anodic areas, depending upon variations in the permeability of the soil, the content of organic substance, the content of sulphides, the content of higher oxides of iron and manganese, the content of oxygen etc., in addition to many other natural factors, such as variations in temperature for instance. It is therefore not normally possible to investigate directly the conditions for the polarization of corroding steel in soil. With the corrosion probe, the magnesium point will always behave as the anode, and the steel pipe as the cathode. Because of the great difference in the electromotive series between magnesium and iron it is hardly possible to have conditions where the opposite could be the case. The normal potential for the reaction is

$$Fe \rightarrow Fe^{++} + 2e^{-} = +0{,}44 \text{ volt}$$

and the normal potential for

$$Mg \rightarrow Mg^{++} + 2e^{-} = +2{,}40 \text{ volt.}$$

The normal potential refers to a pure metal in a 1,0 normal solution of the corresponding ions. In the case of the probe the magnesium anode consists of an alloy of 91 % magnesium, 6 % aluminium, and 3 % zinc + manganese and other impurities. Thus the electrode is not a pure magnesium electrode, and the humidity of the soil has a composition very different from the 1,0 normal magnesium ion solution. In the same way steel does not represent a pure iron, and the solution surrounding it is far from being 1,0 normal with respect to ferreous ions. The difference is, however. not great enough to reverse the relationship between anodic and cathodic parts.

For electrodes in a solution with an ionic concentration different from 1,0 normal we have the Nernst equation:

$$E = E_0 + (RT/Fn) \cdot \ln(a^{n+})$$

E is the potential.
E_0 is the normal potential.
n is the valence of the ion dealt with.
a^{n+} is the activity of the iron in the liquid phase.
F is the faraday (96 500 A sec).

Using Briggsian logarithms and taking a temperature equal to 7° C we obtain:

$$E = E_0 + (0{,}0556/n) \log_{10} (a^{n+})$$

The magnesium ion as well as the ferreous ion is bivalent, thus $n = 2$. Hence we may state that the potential of an electrode of iron and magnesium varies 28 mV for each power of ten by which the concentration of the corresponding ions varies in the surrounding solution.

All the clays from south-eastern Norway are marine sediments. In other countries the sediments may be of different origin. Thus the east Swedish clays and the Baltic clays are sedimented in more or less brackish water. We have no experience with the corrosivity of fresh water sediments, but the results obtained with marine sediments seem to be fully valid even in case of sediments from brackish water. As most marine sediments have been leached subsequent to their deposition down to various degrees of salinity, it does not seem important where the present salinity is below the original one whether the original salinity was high or low. Average ocean water contains 1,272 g of magnesium per litre. This is about a one tenth a 1,0 normal solution with respect to the concentration of magnesium. After sedimentation, and due to the leaching mentioned and adsorbtion phenomena, the concentration of magnesium ions is somewhat altered. However, it seems as if the amount of magnesium is not reduced to the same extent as many be the case with the alkali ions. Even in soils where the leaching has gone very far (ROSENQVIST, 1955) the concentration of magnesium is found to be of the order of 0,1 g magnesium per litre pore-water or more. To a certain extent magnesium-bearing minerals such as biatite etc. may dissolve, thus maintaining a fairly high magnesium concentration. It thus seems as if the magnesium electrode in the soil will have a potential which does not vary more than about 30 mV from one case to another, due to variations in the concentration of magnesium ions in the solution. This means that the magnesium concentration varies between 0,01 and 1 g per litre. In the case of bivalent iron, however, the conditions are different. Ocean water is very deficient in bivalent iron. Consequently an iron electrode which is immersed in sea water will have a potential which is fairly distant from the normal potential, as the concentration of iron may be several powers of ten below normality.

In a soil, however, the content of bivalent iron is normally much higher. Because of the presence of carbonic acid and the absence of oxygen, the various iron-bearing silicates will be slowly hydrolized, and as ferrous bicarbonate is easily dissolved, the amount of of bivalent iron ions may be fairly high, at least below ground-water level. Above ground-water level, where oxygen enters, the iron may be effectively precipitated. In several cases we have formation of hard rust (in Norwegian "aurhelle") on the border line between impermeable clays and more permeable sand and gravel with oxygen-bearing water. Due to the weathering processes and hydrolisis, the content of bivalent

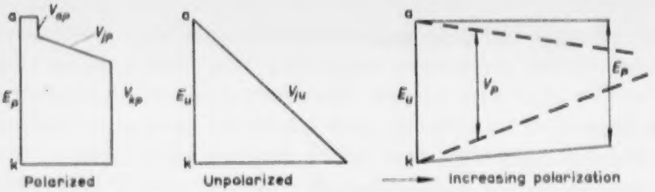

Fig. 26. Schematic presentation of the potential drops and electromotive forces occurring by use of the Norwegian Geotechnical Institute's probe at various conditions.

iron ions in the ground water in the clays may as a rough approximation be considered as constant. This means that the variation is only a few powers of ten above or below the average value. Thus the variation of the potential of the iron electrode will probably be less than 60 mV above and below the average. The other salts which may be present in the pore-water may be considered as constant in the respect that they do not change the activities of the iron and magnesium ions sufficiently to influence the potential of the electrodes. Very seldom has the pore-water less than 1 g of dissolved salts per litre. In the normal corrosive clays the salinity varies between 20 and 10 g per litre. Thus the potential difference between the magnesium and the steel electrode in the unpolarized state may be considered as constant. Even with depolarized electrodes the potential difference may be considered as a function only of the degree of polarizability and not influenced by variations in the dissolved ions.

With our corrosion probe, the measurements are carried out by first reading the resistance in the soil between the pure anode and cathode areas. This is the internal resistance of the element. The reading is taken using an alternating current of 600–1 000 cycles/sec. which is sufficiently high to avoid polarization. After reading the internal resistance, the system is short-circuited through an ammeter of low internal resistance, which is considered negligible in comparison with the other resistance. By corrosion of the magnesium and anodic polarization is brought out on the point of the probe. At the same time the steel surface is cathodically polarized. The drop in potential between the iron and the magnesium will under these conditions be made up of three components, namely:

V_{ap} which is the drop in potential through the anodic layer,
V_{jp} which is the drop in potential through the soil,
V_{kp} which is the drop in potential through the cathodic layer.

The sum of these potential drops will be designated E_p or the electromotive power of the element in the polarized state. V_{jp} is frequently designated as E_p'. E_p may be approximately equal to E_u or the electromotive power in the unpolarized state. Under such conditions the total drop of the potential will take place through the soil (see Fig. 26).

Calling R_a the resistance in the anodic layers, R_j the resistance in the soil, and R_k the resistance in the cathodic layers, we then have the equations:

$$
\begin{aligned}
V_{ju} &= I_u \cdot R_j \\
E_p &= I_p(R_a + R_j + R_k) \\
E_p' &= I_p \cdot R_j \\
E_p'/E_p &= R_j/(R_a + R_j + R_k)
\end{aligned}
$$

The ratio E_p' to E_p in per cent is called "percentage depolarization." This designation is not quite correct, as the value arrived at does not reveal directly how far the anodic and cathodic areas are polarized. However, it does indicate the magnitude of the resistance in the soil between the anode and the cathode. This relationship is a complicated function of the specific soil resistance, and is seen from Fig. 27. Consequently, for a given percentage depolarization there is a greater resistance in the anodic plus the cathodic layer in a soil of high specific resistance than in a soil of low specific resistance. As the transitional resistance in the polarized anodic and cathodic layers is an important factor in the corrosion process, we thus obtain an important parameter in this process. The resistance of the polarized layers increases with increasing corrosion current. If no depolarization sets in, the corrosion current in the stationary medium will build up such a great resistance that it may be considered as infinitely high, i.e. that the current will be equal to zero. The potential drop in the soil will thus also be zero and the depolarization zero.

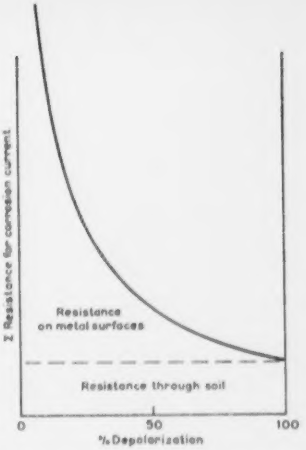

Fig. 27. Relationship between the total resistance in the corrosion probe and the specific soil resistance at various degrees of polarization.

The following example shows the ratio between the sum of the anodic and the cathodic resistance and the soil resistance at various degrees of "percentage depolarization" (E).

$E = 40$ %, i.e. $R_a + R_k = 3/2R_j$
$E = 50$ %, i.e. $R_a + R_k = R_j$
$E = 75$ %, i.e. $R_a + R_k = {}^1/_3R_j$
$E = 90$ %, i.e. $R_a + R_k = {}^1/_9R_j$

We may obtain the approximate electromotive force in the unpolarized state (E_u) when the probe is immersed in diluted sea water containing H_2O_2. On the iron cathode we have nearly complete depolarization, as all electrons will be removed immediately in accordance with the following reaction:

$$H_2O_2 + 2e^- \rightarrow 2OH^-$$

Processes analogous to this reaction are very common when steel objects corrode in soil. It is important to remember that the cathodic and the anodic processes may take place at a certain distance from each other, the iron being dissolved on the areas where the oxidizing power is at the minimum, and the electrons consumed on the most oxidizing areas.

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CHAPTER IX

CORROSION EXPERIMENTS IN THE FIELD

In the literature, a long series of suggestions concerning the measurement and determination of the corrosivity of soils will be found. The majority of these methods depend upon the determination of the conductivity of the soil, in some cases even upon the determination of the cathodic depolarization. In most cases soil samples are examined in the laboratory, though in some few cases field examinations are the basis of the test. In these latter the conductivity seems to be the main object of investigation. As the examinations in most countries seem to be concentrated upon the danger of corrosion of pipe lines, certain factors, as for example the influence of the atmosphere, may be considered constant. Only in a very few, rare cases do we find reference to the corrosion conditions for foundation piles. This is probably the reason why most of the test methods are based upon the readings found by rod electrodes placed at a fairly large distance apart. Various configurations and methods may be used in order to determine the all-over conductivity. Marshall E. Parker (1953) discusses the principle for the various test methods for the determination of the specific conductivity of soils. It is a matter of course that for very long horizontal objects, as for instance pipe lines, variations in the conductivity will be of great importance, and a map giving the conductivity values over a large area will be of the greatest value. However, it is not equally certain that determination of the conductivity values will be a reliable basis for prediction of the corrosion velocity. In the Sovjet Union as well as in the USA various criteria concerning the corrosivity of the soils based upon the conductivity have been set out. Even in Scandinavia such attempts have been made. Thus O. Arrhenius has supported these criteria, and has predicted very high corrosion velocities in several localities. Even though there may be a certain variation between the different asumptions about the relationship between velocity of corrosion and conductivity, the similarities between the opinions of the various authors are most striking.

We have tried to collect some of the average values for the criteria which are most frequently used in Scandinavia, namely the American and the Russian ones. Table 5.

If these criteria are compared with the average values of the conductivity of the east Norwegian marine clays, which are seen in the table, corrosion velocities above

TABLE 5.

Conductivity groups and approximate corrosion rates compared to the conductivity of Norwegian marine clays.

Corrosivity	Approximate corrosion rates	Specific soil resistance R in ohm cm	
		USA	USSR
Very high	> 1 mm per year	0– 100	0– 500
High	0,2–1 mm per year	100–1 000	500– 2 000
Normal	0,05–0,2 mm per year	1 000–6 000	2 000–10 000
Low	< 0,05 mm per year	> 6 000	> 10 000

Estimated conductivity of marine clays of eastern Norway:

ca. 10 %	19[1] – 50 ohm cm
ca. 25 %	50 – 250 ohm cm
ca. 20 %	250 –1 000 ohm cm
ca. 20 %	1 000 –5 000 ohm cm
ca. 25 %	> 5 000 ohm cm
100 %	

0,2 mm per year are to be expected in about 55 % of all cases. Only in 25 % of the cases should corrosion velocities below 50 microns be expected. Consequently, these criteria are in most marked opposition to the actual findings in the sub-soil of eastern Norway, whereas they seem to tally very well with the corrosivity in the top soils. Most probably the young origin of the Scandinavian marine clays is the reason why the top soil and the deeper strata behave in such different ways. If the criteria which are mentioned above should happen to be correct, it would mean that normal foundation piles would disappear completely in the course of about 50 years in a great part of the Norwegian soils. However, as seen below we have extracted piles from soils where the specific resistence was less than 150 ohm cm, and have found on examination that the corrosion even in these cases has been very low.

Below we give some case records in order to elucidate the corrosion experiments upon which our methods are based.

Case records.

The Nurses' Home, Drammen.

In 1954 a new building was built to house the nurses at the Drammen Community Hospital. The ground consisted of marine clay deposits, which were relatively highly weathered in the upper layers. By means of an old type corrosion probe of the Norwegian Geotechnical Institute, the soil characteristics given in table 6 were found.

The instrument used most probably had som zinc left on the steel pipe electrode, which led to depression of the driving voltage, between the magnesium point and the steel electrode, by about 0,5 volt. Thus the maximum value for this particular corrosion probe seems to be of the order of 700–750 mV. We regret that we did not take all necessary measurements at that time, but in 1954 our knowledge of the influence of various factors was not so advanced as we think it is to-day. Based upon these very uncertain values we assumed that the depolarization varied between 70 and 35 %, and even though the values were not regarded as very serious, we decided upon installing electrical corrosion protection. Buried graphite anodes at a total current of 8–10 amp. and a terminal voltage of 3–4 volt were employed. Simultaneously, four control rods were driven in the ground. Two of these were coated with asphalt, and two of them left as they were. One of the coated and one of the untreated rods were connected in a circuit of the electrical protection installation, whilst the other pair were left out of the system. After five years, in February 1959, the four control piles were extracted and examined. It was found that parts of the non-protected piles had suffered severe corrosion, whereas the two piles connected with the protection installation had suffered no visible attack. The piles were marked A, B, C, and D, A and B being the two piles connected with the electrical protection system, C and D the piles left out. Pile C was the untreated one, pile D the coated one. Examination of the piles gave the following picture:

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[1] Swedish west coast.

Pile A and B: No visible attack.

Pile C: The upper 30 cm, no visible corrosion; cross section 22.1 to 22.3 mm. From 30 to 45 cm pitting. Pits, up to 1.5 m deep, varied between6 and 1 cm² in size. From 45 to 90 cm, slight attacks. From 90 cm to 1.5 m, pile evenly attacked; cross section 21.8 to 22.1 mm. The surface in part had acquired a spongy appearance, due to minute pits. From 1.5 to 2.0 m, still more evenly attacked; cross section 22.0 mm. From 2.0 and downwards, no visible attack; cross section varied between 22.2 and 22.0 mm.

Pile D: The upper 50 cm, no pronounced attack. From 50 to 60 cm, pitting; depth up to 1.5 mm. From 60 cm to 1.30 m, separate pits of the same depth. From 1.30 to 2 m, numerous pits; depth up to 1 mm. From 2.0 m to 4.0 m, slight attacks; cross section 22.2 mm. From 4.0 m down to the point of the pile (6 m) the pile was evenly attacked; cross section 21.8 mm.

On the basis of this inspection therefore, we may conclude that the cathodic protection equipment had been fully effective. The potential measurements carried out at the site proved that the potential of the protected piles was – 1 000 mV against a copper/copper sulphate half cell, whereas the coated pile which was not protected had a potential of– 450 mV, and the non-coated pile had a potential of somewhat above–600 mV against a copper/copper sulphate half cell.

TABLE 6

Depth m	Specific resistance ohm cm	Effective voltage mV	Depth m	Specific resistance ohm cm	Effective voltage mV
1	396	566	11	663	381
2	426	531,3	12	721	369
3	569	418	13	975	297
4	594	443	14	786	332
5	458	413	15	786	429
6	435	427	16		
7	585	450	17	607	414
8	407	422	18	721	342
9	474	413	19	804	329
10	488	375	20	826	317

The high potential for the coated pile indicated that the corrosion must have been intensive in the places where it took place. Accordingly, it seems that the asphalt cover was of no value, and may even have concentrated the attack in certain areas. The amount of iron which had been dissolved on the coated piles did not seem to be much less than the amount of iron which had been dissolved on the non-coated pile.

A/S Thor Dahl, Sandefjord.

The foundation of the office building of this firm of ship owners in Sandefjord was the object of thorough investigations. The examination of the electrical properties of the soil, was carried out by means of the Norwegian Geotechnical Institute's corrosion probe. The results are given in table 7.

TABLE 7

Depth m	Specific resistance ohm cm	% depolarization	Depth m	Specific resistance ohm cm	% depolarization
1,3	1810	55	15,5	64	53
2,5	291	73	16,5	68	57
4,5	72	51	17,5	67	55
5,7	61	70	18,5	71	55
6,5	80	73	19,5	65	53
8,5	78	78	20,5	69	58
9,5	63	51	22,5	74	57
10,5	86	70	24,5	100	50
11,5	89	63	26,5	88	62
12,5	84	70	28,5	77	62
13,5	67	49	30,5	208	70
14,5	79	59			

From the surface down to 1,2 m, the ground consisted of fill, from 1,2 m to 6 m, of clay with a high content of organic material, from 6 m down to the bedrock, of silty clay with bits of seashells and some traces of gravel and small stones. The water content throughout was below the liquid limit, and varied around 45 %. The liquid limit varied between 50 and 60 %, the plastic limit between 20 and 27 %. The profile gave geotechnical data corresponding to a normal consolidated clay, with an increase in undrained shear strength of 0,2 times the effective overburden. Based upon the investigations of the chemical and electrical properties, it was included that the soil was corrosive, and in our report to the firm it was stated as our opinion that the average life of a normally loaded H-beam pile should not be considered as more than 50–70 years. In the same report it was stated that localized corrosion might be feared at the places where the piles were welded, as stresses in steel during welding are inevitable even when soft electrodes are used.

"Steel subjected to mechanical stresses will behave as a less noble metal than steel of a corresponding composition without mechanical stresses. We consequently have to take an increased corrosion in the zone adjacent to welds into account. Unfortunately we have not sufficient data to state with certainty the life time of a normally loaded steel pile. However, we may not exclude the possibility that such a pile under the conditions found may be attacked at a velocity of 1,5 mm per 10 years. This will bring the pile to failure after 50–70 years.

This conclusion is only based upon analogies. We have not sufficient material for comparison, and we do not know the nature of the welds performed. We may possibly expect deviations in both directions."

In the autumn of 1957, Mr. Winge *Simonsen*, who is managing director of the firm of ship owners to which the building belongs, presented the Norwegian Geotechnical Institute with a gift for which we were very grateful. He allowed us to extract a 32 m long steel pile, one of those on which the neighbouring building had been founded. This pile, which had been driven in 1946 and consequently had been in the ground for 11 years, was cut up for examination of the state of corrosion. When the pile was extracted, visual examination proved that the corrosional attack had been very severe. The following notes were taken on the spot during pulling. The depths in metres refer to the distance from the top of the pile, which was situated 180 cm below the surface and 80 cm below ground water level.

0– 1 m severe corrosion, pits up to 6 mm depth over extended areas.
1– 2 m strong corrosion and pits.
2– 3 m a weld in this area somewhat corroded; the pile slightly corroded; grey cathodic cover.
3– 4 m severe corrosion, pits up to 5 mm depth; much cathodic precipitant.
4– 5 m much precipitant, especially on both sides of the weld which is attacked strongly.
5– 6 m some few pits, some cover.
6– 7 m some attack, mainly harmless.
7– 8 m considerable attacks, especially around the weld; cathodic cover around the weld.
8– 9 m one pit, 5 mm in diam. and 1 mm depth; grey cover surrounding the pit.
9–10 m some shallow pits, grey cover around.
10–11 m small pits, depth about 1 mm; the weld severely attacked; cathodic cover.
11–12 m no visible attack; millscale intact.
12–13 m extended pits over large areas, depth about 1 mm, especially on one flange.
13–14 m the weld at a depth of 13.15 m attacked; the attack continued down to 13.5 m.
14–15 m slight attack, some cover.
15–16 m some pits, depth about 0.6 mm; at 15.8 m, thick cover and pits 1 mm depth.
16–17 m cover and some attack down to 16.6 m.
17–18 m a large area with an attack of 0.5 mm on one flange, the other flange relatively unharmed.
20–21 m no visible attack; the pile seems intact.
21—22 m some attack at the weld, the rest seemingly unharmed.
22–23 m at 22.7 m one small pit surrounded by grey cover on one flange; on the other flange some pits of 0.5 mm depth along the whole cross section at a length of 30 cm.
23–24 m some cathodic cover, seemingly unharmed.
24–25 m much cathodic cover, attack on both sides of weld; at 25.0 m, one extended pit 0.5 mm deep.
25–26 m large areas with 0.2 mm deep pits on one flange; the other flange seemingly intact.
26–27 m at 26.15 m, shallow pits, much cathodic cover; the rest of the pile seemingly intact; some cover.
27–28 m attack at weld, cover around it.
28–29 m large shallow pits on half of one flange for a length of 25 cm; the rest seemingly unharmed.
29–30 m seemingly unharmed to 29.8 m ,then some pits of 1 mm depth over an area of 50 m^2.
30–31 m some pits on one side of the weld.
31–32 m some shallow pits on one flange; the other flange some few pits and some cover.
32–32.8 m much cathodic cover; some even attack, and some concentrated attack at the point.

When the pile was drawn it had to be cut up into bits of about 3 m length. In order to carry out further investigations, samples had to be brought to the laboratory. These were taken at the end of each of the arbitrary bits cut during the pulling. Thus the samples brought for laboratory examinations were not subjected to any preferencial selection. In addition to these arbitrary test samples, we cut out special samples in places where the corrosion picture was particularly critical, either due to pitting or to localized corrosion in the neighbourhood of welds. The test samples were brought to the laboratory and sand blasted in order to remove loose cover. Experience has shown that mild sand blasting does not attack the steel to any great extent, so that the measurements of the thickness of the sand blasted pieces ought to be representative of the thickness left after corrosion. In this case we had no accurate measurements of the dimensions of the pile before driving. The only thing we knew was that the pile in this case was a Bethlehem steel product and in accordance with the US Steel Company's norms for an 8″ Wide Flange pile. According to these norms, the thickness of the flanges ought to be 17,35 mm, and the web 10,29 mm. Normally the tolerances for commercial steel permit a slight excess of the standard dimensions. This is especially the case for rolled profiles. When the sandblasted pieces were examined by micrometer, however, it was found that in most cases the dimensions were below the norms. Each piece was measured in at least 10 different places. Frequently, as many as 25 single measurements were taken on each flange and upon the web, and the average of these measurements is given below. In order to examine typical pit attacks, a special micrometer-clock was moved along a plain parallel frame which was placed directly upon the steel, thus lying upon the highest parts. The point of the micrometer had a diam. of 1,5 mm. Thus only pits larger than this cross section were measured. For smaller pits, measurements with a penetration needle were carried out. As an approximation we may assume that the largest average thickness found for any test sample is representative of the thickness of the steel before driving. We arrived at the conclusion that even pieces which seemed to be unharmed had suffered very even decrease in thickness. This decrease in thickness seems to be a reality even though visual examinations did not indicate attack. It seems that the largest all-over loss of steel occurred just in the cases where no pronounced pitting had taken place, whilst the maximal thickness of flanges and webs were found around deep pits. These maximal thicknesses were equal to or even above the standard dimensions for 8″ WF piles. Thus it seems as if the attack in the pits themselves to a certain extent had protected the steel sorrounding the pits; the steel in the pits having acted as sacrificing anodes (Fig. 28 a-b-c).

In addition to the all-over attack found in many places, we have already mentioned that the surface of the steel had acquired a spongy structure, with micro-pits, of cross section less than 1 mm^2, close to each other. The depth of these micro pits is up to 1 mm. This spongy structure has nothing to do with a primary defect in the steel, but seems to be due to a special type of corrosional attack.

As for the all-over attacks, they had been so even in some places that they had not removed the marks from the rolls in the steel mill. On several of the test pieces we still could read the name "Bethlehem." These parts seem to be quite analogous to a coin dissolved in an acid. It is well known that a coin may be dissolved so far that only a few

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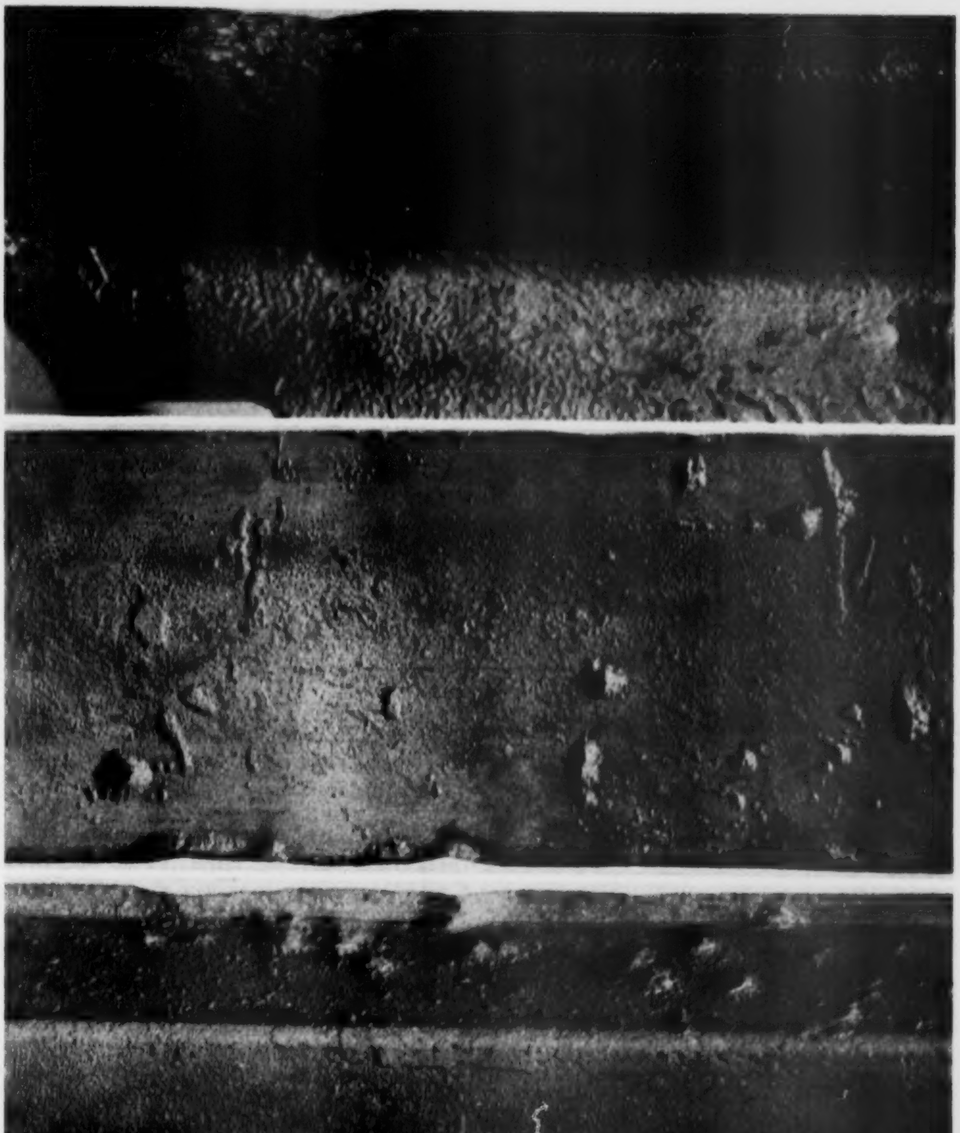
Fig. 28. Foundation steel pile from Sandefjord showing a) severe corrosion on the flange (from below) and deep corrosion pits on the flange, b) from above, and c) from below.



per cent of the original thickness is left, and still it is possible to differentiate head from tail.

The measurements of the thickness, based upon 10–20 micrometer readings, were all taken on those areas of the pile where no special pitting was seen, and thus gave the average value for the seemingly best parts of the piles. When the bearing capacities of the piles are calculated, the localized attacks must be taken into account, thus giving lower values than would be based upon the readings below.

Result of readings:

Depth m	Flange 1 mm	Flange 2 mm	Web mm	Remarks
1,00– 1,50	16,80	16,51	10,73	In addition to an all-over attack, localized pitting both on flanges and web has occured. In some areas the surface is spongy.
3,50– 3,60	17,19	16,75	10,55	On one flange a large area is considerably more attacked than average; the other flange much less harmed, except for some few micro-holes. Even on the web some of the micro-holes are seen.
6,80– 6,90	17,28	17,23	10,54	Test piece even, on both flanges and web.
10,05–10,15	16,46	16,68	10,72	Test piece even, on both flanges and web.
13,12–13,42	16,44	16,45	10,52	In this test piece there is a weld, and especially on the one side severe corrosional attack is found. Immediately adjacent to the weld seam there is an even corrosional groove 2–3 mm deep. Thus the cross section of the steel in this flange is reduced by about one quarter. Farther away from the weld, some larger shallow pits are seen.
16,50–16,60	16,47	16,49	10,55	On one flange and on the apex between flange and web slight attack may be seen. On the other flange minute attacks. Otherwise, sample fine.
19,70–19,80	17,74	17,86	10,43	Test sample mostly even and seemingly unharmed.
23,00–23,07	17,65	17,65	10,45	On one flange some attacks above average, otherwise fine.
26,20–26,27	16,59	16,62	9,87	Especially on one flange there are noticeable attack phenomena on the inside, against the web. The other flange has acquired a spongy structure and the web has some irregular attacks, but on the whole the sample gives an even impression.
29,25–29,35	16,61	16,59	9,94	Somewhat spongy structure in one flange, the rest mostly even.
32,55–32,85	16,59	16,56	9,93	The pile has been broken during ramming, and the point is missing. The broken end, which has supported the pile against the bedrock, is somewhat deformed and slightly attacked by corrosion.

Depth m	Flange 1 mm	Flange 2 mm	Web mm	Remarks
		Special samples.		
3,30– 3,50	17,20	16,97	10,73	On one flange there is a longitudinal groove 3 cm across and 2,5 mm deep. On both sides of this groove the surface is spongy.
27,50–27,70	16,63	16,57	9,98	This sample was taken out because of the weld. Across the web is a 2 mm deep groove on both sides of the weld seam. Thus nearly half of the steel cross section in the web is lacking. Both flanges seem quite spongy on the surface, and adjacent to the weld seam even the flanges have suffered coarse attack. This weld seems to be of inferior initial quality, possibly there have been some electrical difficulties, and perhaps some abnormal heating during welding. In spite of these corrosional attacks the engraving from the rolls could still be read at a point 6 cm from the seam.
0,75– 1,00	16,63	16,97	10,71	In this sample there are the most accentuated corrosinal phenomena. In some places the pile seems mouse-eaten, and the attack has been 6 mm. The fibre direction in the steel is visible, and the stress trajectories crossing each other at 45° to the axis of the pile are visible. The corrosion has left marked striations in these directions. The middle part of the pile is quite pock-marked by pitting.

Looking at the values found for flanges and webs, we find that these may be above as well as below the norms for 8″ WF. As previously stated, the standard thickness for the flanges is 17,35 mm, and for the web 10,29 mm. These values represent the normal minima. Because of wearing in the rolls, these minima generally are exceeded, and it seems reasonable to assume that the steel originally had dimensions corresponding to the highest values found by us, i.e. flange 17,86 mm and web 10,73 mm. These values represent average values on a test piece, whereas the highest single values found by micrometer reading were still somewhat above these averages.

Assuming that the beam originally had these dimensions, we found that the attack at some places had reduced the flanges by 1,4 mm, and the middle parts by 0,8 mm, corresponding to an all-over corrosion of 0,7 and 0,4 mm. In addition there is the corrosion in the pits and at the special places. As this steel pile had been in the ground only for about 10 years, we have an all-over attack in the worst places corresponding to 0,07 mm per year, for normal pile foundations for housing etc. corrosional attack of about 0,02 mm all-over per year is considered the permittable maximum.

Of special interest is the attack adjacent to the weld seams. While some of the weld seams did not seem to have suffered localized attack, others had marked corrosion on one or both sides.

As there was a possibility that the weld originally was somewhat weak, we had X-ray control carried out by the firm Røntgenkontrollen. The X-ray picture is seen in

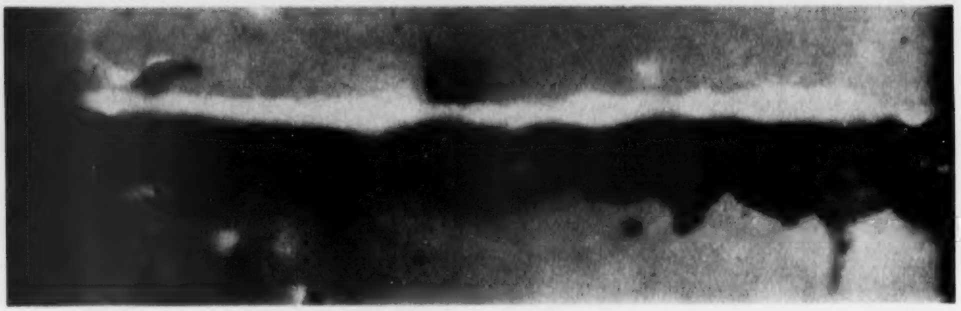


Fig. 29. X-ray picture of the web of a welded pile, showing localized corrosion along the weld. Scale 1 : 1.2.

Fig. 29. The control laboratory gave mark 3 as the quality of the weld. This means that smaller discrepancies existed in the homogeneity of the weld caused by one of the following errors, or by a combination of them: a) pores, b) enclosed slag, c) edge discrepancies, d) root discrepancies.

Thus the weld seems to be neither particularly good nor bad. Consequently we have to assume that the major part of the loss in dimensions found is due to corrosion, and not especially to a bad weld. The result of the investigation of the extracted pile thus is in complete conformity with the conclusions arrived at in 1954, based on laboratory investigations and determination by the corrosion probe.

Experiences from Gothenburg.

Allan Bergfelt (1957) published the result of some investigations concerning the corrosivity of steel piles and a dolphin in Gothenburg. In this case, measurements with the corrosion probe from the Norwegian Geotechnical Institute were carried out before the piles and the dolphin were drawn. The type of corrosion probe which was used during these examinations was somewhat different from the present model, and the values published by Bergfelt consequently have to be calculated in order to compare the values with those published elsewhere in this paper. In the case of the dolphin published by Bergfelt the readings listed in table 8 have been obtained.

TABLE 8

Depth	*p*H	Specific resistance ohm cm	Depolarization %
0 to −3,5 m water			
No measurement.			
− 4 m silty clay	7,9	350	No measurement
− 5,5 m grey silty clay	8,3	180	42
− 6,5 m	8,3	180	50
− 7,5 m	8	180	51
− 8 m	8,2	180–210	50
− 9 m	8	230	62
−10 m	8	200	63

The sensitivity of the clay was low, about 4. The dolphin, which was 26 years old when it was drawn, proved to have undergone an average corrosion in the water of about 1 mm between 1 m below mean water level and the bottom of the river, and corrosion varying between 1/10 and 1/5 mm from the river bottom to the undermost part of the dolphin, which was 9 mm below water level. Certain maxima just below the river bottom and at a depth of 8 m were seen.

Another case dealt with by Bergfelt is in a harbour shed called Lindeholmskjulet. In this case the specific resistance was very close to 300 ohm cm, with a minimum value of 150 ohm cm at 7 m depth, and a maximum somewhat above 300 ohm cm at a depth of 8,25 m. The degree of depolarization was fairly constant, varying between 44 and 47 % of the maximum value. The content of chloride coresponded to 10 g per litre pore water. The extracted pile gave few signs of corrosion. In some places it might be as much as 0,2 mm. The only localized attack was at a depth of 8 m, just where the steepest gradient in resistivity was found. Here localized attack to a depth of 0,5 mm was found. Thus these piles from Gothenburg clearly demonstrate that low resistivity is not a sufficient criterion for suggesting strong corrosion. Even in these soils, where sulphate-reducing bacteria are present and sea water with its high content of sulphate fills the pores of the clay, moderate to very low attacks may be found. In this case, the low degree of depolarization found by the corrosion sonde tallies very well with the actual findings.

Uglum Bridge, Gothenburg.

At the railway bridge crossing the Säveå, 7 km outside Gothenburg, a 21 m long test pile consisting of 19 mm steel boring rod was driven in 1938. After 18 years this pile was drawn and examined, after examination of the ground by means of the Norwegian Geotechnical Institute's corrosion probe. See table 9.

TABLE 9

Depth m	% depolarization	Specific resistence ohm cm	Depth m	% depolarization	Specific resistence ohm cm
2,5	66,7	800	12,0	75,3	115
3,0	69,3	520	13,0	77,9	114
4,0	69,0	295	14,0	75,6	112
5,0	77,0	210	15,0	76,6	118
6,0	79,0	160	16,0	79,4	123
7,0	76,3	150	17,0	77,2	130
8,0	78,5	145	18,0	77,0	132
9,0	82,5	127	19,0	74,7	140
10,0	83,5	125	20,0	73,0	137
11,0	77,2	115			

The pile proved to be very slightly attacked, averagely less than 0,2 mm corresponding to about 0,01 mm per year. Pitting was not observed. Six measurements were taken for each metre of the rod. The only place where some uneven corrosion could be observed was between 10,5 and 11,5 m. Here there were variations from a high degree of depolarization of 83,5 % at 10 m to 77,2 % at 11 m. In this case the soil was rich in sulphides, and the high depolarization values found by the probe probably are due to bacterial activity.

Even so, the soil of very low specific resistance and with active bacteria had not harmed the steel to any great extent during 18 years. The relatively high depolarization found in this case has not proved to be as harmful as in cases where the same instrumental reading is due to inorganic processes. There seems to be a difference between the propagation of bacterial depolarization and inorganic depolarization in dense clays. In more pervious soils, such as sand and gravel, bacterial activity may be much more harmful. It seems as if the values found by the corrosion probe in such sulphide-bearing clay depend upon the present bacteria immediately surrounding the zone. The mobility of the bacteria and the nourishing salts in the dense clay must be very low, and do not allow the instantaneous attack to continue with any high velocity.

In the case of Uglum Bridge the clay is situated in a horizontal plane, and the hydrolic gradients must be very low, so that the water phase surrounding the pile must be regarded as stationary.

This example is to-day the only one we have found which demonstrates clearly that not only the electrical reading found by the instrument, but the general topography and the permeability of the clay have to be taken into account when the corrosivity of an area is to be evaluated.

Test piles of the Norwegian State Railways.

As earlier mentioned, the Head of the laboratory of the Norwegian State Railways, Chief Engineer Sverre Skaven-Haug, had installed accurately measured test piles at different places in the Southeastern Norway. He kindly permitted the Norwegian Geotechnical Institute to examine the soil by means of the corrosion probe before the piles were drawn. The following three localities represent three different types of soils. As the findings are in general agreement with all the other examinations carried out, it is unnecessary to give more than the three cases.

Hafslund near Sarpsborg.

The depolarization varied between 48 and 60 %. The resistivity was fairly constant, and high, varying between 2 500 and 3 500 ohm cm. Thus this locality represents high resistivity and low depolarization. The average corrosion of the pile after 17 years was found to be between 0,1 and 0,2 mm. The soil consisted of silt.

Oslogate, Oslo.

The specific resistance varied between 230 ohm cm and 40 ohm cm. The depolarization varied between 81 % and 45 %. None of the variations were abrupt. The pile which was withdrawn had been in the ground for 18 years. The average corrosion was about 0,4 mm with a minimum of 0,1 mm in a depth of 4 m, and a maximum of 0,5 mm in a depth of 5,5 m, a locality with fairly low depolarization and low resistivity. The soil consisted of clay.

Persgangen, Oslo.

The specific resistance dropped from 350 ohm cm at a depth of 2 m to 40 ohm cm at a depth of 8 m. The depolarization increased from 42 % at a depth of 2 m to 77 % at a depth of 3,5 m. This value kept constant down to 5,5 m, decreased to 60 % at a depth of 7 m, and kept fairly constant at this last value in the deeper strata. The average corrosion on the pile, which was 6,5 years old, was 0,7 mm. At a depth between 4,5 and 5,5 m the average corrosion was much higher, and the maximum corrosion here was about 2 mm. In this case the ground, which consisted of clay, had high depolarization and low resistivity.

These three examples clearly demonstrate the importance of comparing resistivity and depolarization values. In all cases the soils were much coarser than that at Uglum Bridge, Gothenburg. The hydraulic gradients may be somewhat steeper in the last cases. though none of the localities was situated on a typical slope. The high corrosivity at Persgangen tallies with the instrument reading from which we would have advised against the use of unprotected steel piles. The result of the investigations is seen from the Fig. 30.

The factors which we have found to be of the greatest importance for corrosion in steel piles are:

a. The various types of depolarization.
b. The electrical conductivity.
c. Variations in the salinity in the direction of the pile.
d. Variations in the content of oxidizing matter.
e. Variations in the temperature.
f. The mobility of the water phase in the soil.

All these factors are measureable by means of electrical instruments. In order to facilitate the interpretation of the various factors we have tried to separate the soils in five groups, according to the expected rate of corrosion:

Corrosion group 1:	< 0,001	mm per year
Corrosion group 2:	0,001–0,005	mm per year
Corrosion group 3:	0,005–0,02	mm per year
Corrosion group 4:	0,02 –0,1	mm per year
Corrosion group 5:	> 0,1	mm per year

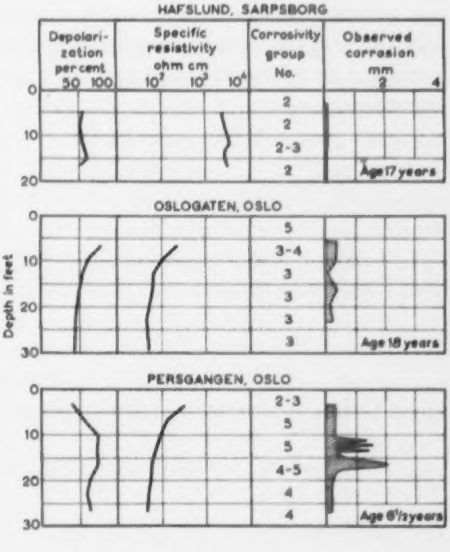


Fig. 30. Results of in-situ measurements with the corrosion probe at three different sites, where actual corrosion was observed on steel piles.

For depth of corrosion we have set up the following definition: "The average depth corresponding to the loss of iron on any surface of a size of 500 cm²."

In a great many cases corrosion attacks on steel piles take place as localized pitting. In normal steel piles a single pit does not impair the bearing capacity of the pile to any great extent. In cases, where the pits are clustered together, the effect will be nearly analogous to that resulting from an even attack. We thus assume that if an area of the order of magnitude 500 cm ^{2} is attacked beyond a certain extent, the bearing capacity of the pile will be significantly reduced. It is immaterial whether or not the rest of the pile is attacked.

As to the relationship between the depth of the pits and the average loss in weigth there are many values given in the literature, and this ratio must be said to be very variable. Nevertheless, the values given seem to vary mainly between two and ten times the average depth of corrosion as calculated from the loss in weight. Schwerdtfeger and McDorman (1951) has compared the results obtained fro msteel and cast iron which has been buried for 10–12 years. He gives a formula for the ratio between the pitting depth and the avrage after ten years. His formula runs as follows:

$$P_{10} = 5{,}2 \cdot W_{10} + 36.$$

In this formula P_{10} is the maximal depth of pits in thousands of an inch on an area of a cross section of 0,4 ft^2 (360 cm^2), and W_{10} is the loss in weight in ounces per ft^2. When this formula is recalculated in metric units, it gives the depth of the pits as between 2,5 and 3 times the average corrosion depth which is calculated from the loss in weight.

This empirical value seems to fit in with the experiences found in Norway. By empirical calibration of the corrosion probe we have tried to take the ratio between the pitting and the average attack in account. We have given our values a safety factor which we asssume to be of the order of 3 for the case of an even attack. Except for this additional safety, the relationships between the measurements taken by the probe and the degree of corrosivity are entirely empirical, based upon a hypothetical formula and the results found from steel piles, test rods, archaeological finds and steel objects which have been subjected to corrosion in sea water or in soil. The relationships are based chiefly upon our own experiences, but a certain use has also been made of values taken from the literature.

CHAPTER X

CATHODIC AND ANODIC PROTECTION

a. Cathodic protection.

In most metal/liquid systems there is a tendency towards corrosion, as the system represents a thermodynamic state of higher energy than the corrosional products which may arise. Generally in such systems we may divide the *p*H potential field into various areas, as done for instance by Pourbaix in the well-known Pourbaix diagram, given on page 20 (Fig. 12). As will be seen, the pH/E_H field is divided into three areas; that including the whole *p*H scale at a sufficiently low potential, called the immune field, that which depends highly upon the *p*H, called the passive field, and those between these two, the corrosion fields.

According to such a diagram the corrosion of iron in normal water or soils at *p*H values between 5 and 9 depends upon the existence of a "dangerous triangle" in the potential *p*H diagram. The iron may be protected against corrosion if the *p*H and the potential are adjusted in such a way that the iron represents a point outside the "dangerous triangle." However, we may also change the chemical composition of the surrounding medium, as for instance demonstrated by Pourbaix in the Pourbaix diagram where an inhibitor such as potassium chromate is present, see Fig. 13. In case of steel piles in soil such a procedure is hardly possible. For steel in concrete, or in ditches, as for instance in pipe-lines, it may be possible to achieve protection by adding inhibitors to the medium, though to our knowledge this has never been done in Scandinavia.

For the reasons mentioned the following four methods are available for protecting iron against corrosion:

1. We may adjust the *p*H to values between 9 and 12.
2. We may lower the potential to values which bring the steel within the immune areas (cathodic protection).
3. We may increase the potential sufficiently to bring the steel into the passive areas (anodic protection).
4. We may add some chemicals which protect against corrosion by some kind of chemical sorbtion (inhibition).

Cathodic protection was used as early as 1824 by Sir Humphrey Davy who demonstrated that less noble metals (zinc) protected the copper of the British warships against corrosion due to the depression of the potential of the copper platings. In this country cathodic protection has been especially important in two fields, namely the corrosion of ships, and the corrosion of steel in soil.

At the Norwegian Geotechnical Institute we have worked especially with problems belonging to the last-mentioned category.

The increasing prices for steel and labour have made corrosion protection a field of increasing interest from an economic point of view. It is less than 30 years ago since cathodic protection gained any importance outside the laboratory. To-day, corrosion in various forms costs between 100 and 1 000 kroner (equal to $15 to 150) per year for each inhabitant in the industrialised countries. During the last three decades scientists and technicians have developed a protectional technique. Although the technology and the theoretical basis of the various forms of corrosion protection is still insufficiently known, the application has been carried out successfully.

Investigations which have been undertaken by the Norwegian Geotechnical Institute seem to indicate that the subsoil in Scandinavia will usually be harmless in cases where normal building foundations are considered. Even unprotected H-profile piles or similar types of foundation with slender steel members may be relied upon, provided the building is not expected to have an extraordinarily long life-time. With monumental buildings such as churches, town halls etc. matters are naturally otherwise.

In case of pipe-lines conditions are quite different. Such constructions are placed in ditches, dug for the most part in the topsoil. Air and other oxidizing agents are allowed to penetrate, and the chemical conditions may vary considerably along the line. In other countries, where the subsoil has a composition entirely different from the topsoil, we may expect higher corrosivity for foundation piles in the subsoil. Although concrete piles or pipes may be used with advantage, it will sometimes be most convenient to use steel, when it is of the greatest importance to increase the life-time of the construction, either by coating, which prevents the entrance of the aggressive liquid phase, or by some kind of electric protection, mainly the cathodic one.

The great value of the cathodic protection method lies in its simplicity and effectivity. The aim is to lower the potential of the construction below the border line in the Pourbaix diagram which separates the immune area from the corrosive. In pipe lines this may be done by placing anodes at suitable distances from the pipe along the section which is to be protected. For corrosional protection we may use either sacrificial anodes to provide sufficient electrons, or we may add these from an external source. The first method is called conventionally galvanic protection, and the second electronic protection. The different terms merely distinguish the method by which the electrons are provided; either by a process which may be compared to that in a normal torch battery, or in the second case from an external energy source, which may be a water-fall, a motor or steam engine via a generator, transformer, or rectifier. In both cases it is the electric energy which forms the barrier prohibiting the formation of local cells on the protected surface. When the electric corrosion currents are stopped, the corrosion process will stop simultaneously.

To-day, an extensive literature dealing with cathodic protection exists, and a long series of firms has specialized in such protection installations. Cathodic protection installations were installed on a great scale before the last world war in the USA and in Soviet Russia. According to V. A. Pritula (1953) cathodic protection was first used in the Soviet during the years 1923–1928 in order to protect underground pipe lines. At the end of the thirties and the beginning of the forties the number of installations increased rapidly on account of the great economic savings which had been observed by the first installations. A corresponding development has taken place in the USA, mainly in the thirties and forties, when cathodic protection was installed on a great scale on pipe-lines, mainly for oil and water.

In order to design the size of an installation for cathodic protection it is necessary to carry out drainage tests, and determine the polarization and changes in potential of the metal construction against the surrounding soil. Several methods have been developed. The majority are based in principle upon the determination of the difference in potential between the construction and some kind of standard cell. Diagrams are drawn for the variation of the potential as a function of the applied current. In this case the current density distribution along the construction is of great importance. In Norway and most other places it is normal to use a standard copper/copper sulphate electrode as reference. In principle it is correct to place the reference electrode as close to the construction as possible but with media of relatively high conductivity this point is not always critical (Fig. 31).

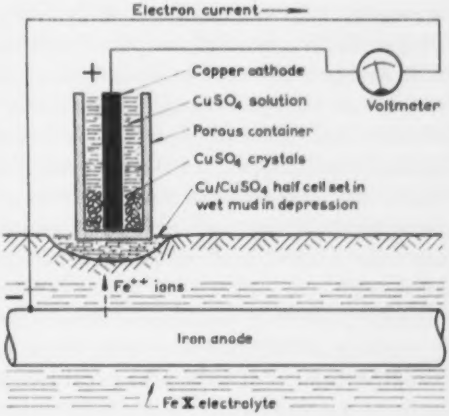


Fig. 31. The principle of measuring the potential of corroding steel by means of the copper/copper-sulphate half cell.

For the practicing engineer it is of interest to know how much such an installation will cost. It is not possible to state with certainty which type of installation will be the cheapest and most economic. We may either use sacrificial anodes of an ignoble metal such as magnesium or zinc, or we may use an external source of electricity combined with different types of anodes. They may be either resistant towards corrosion, such as graphite or carbon or platinated titanium, moderately corrodible such as ferreous silicium. or lead alloys, or they may be easily corrodible such as scrap iron or other scrap metal. The use of sacrificial anodes made from an ignoble metal like zinc or magnesium has the advantage that the cost of installation is low, whereas the provision of an external source for electricity will normally involve high installation costs; in the last-mentioned case however the cost of maintenance will be much lower than with sacrificial anodes. The method to be recommended thus depends upon th price for electricity and the size of the construction, as well as upon the corrosivity.

In some cases other factors have to be taken into account, as for instance in oil tankers where the danger of explosion prohibits the use of external sources. For safety reasons we have to choose the most expensive method in this case, namely sacrificial anodes, although impressed direct current and permanent anodes might be much cheaper. It is not permitted to have any risk of sparks in tanks which may contain explosive gasses, and with impressed current the voltage will normally be so high that a poor contact or a break in the lines may cause a disaster.

In case of subsoil constructions of steel, as for instance piles, the price of the anodic metal, the nature and composition of the building ground and several other factors have to be taken into account. Only in very small installations does it seem to be justifiable to use sacrificial anodes, for instance of magnesium. For piles, we have arrived at the conclusion that provided the total surface of the metal to be protected from corrosive soil is 100 m^2 or more, the impressed current method is preferable. We are generally using external sources of electricity and buried graphite anodes, and have found this to be the cheapest method. It is dangerous to give any prices for the cost of a protectional installation compared to the total cost of the foundation, but in most cases it seems as if the cost of the protectional installation will be small compared to the other expenses; a ratio of 1:10 to 1:30 seems to be fairly common in the case of pile foundations. This means that if a part of the piles could be ommitted because of the protectional installation, the total cost will be actually lowered through such an installation. With steel pipes as well as with pipe-lines, great amounts of steel are used only because of the danger of corrosion. The steel pipes have got much thicker walls than necessary for the pressure of the liquid, and the piles are normally loaded to less than 1 200 kg/cm^2, although they might very well be loaded up to 2 000 kg/cm^2 from purely structural considerations. The permissable stresses are kept low because of the danger of corrosion. If we could rely upon the protectional installation, between one third and one half of all steel bearing piles might be omitted, or more slender profiles might be used. Of course, in every cathodic protection installation some control in order to ascertain that the installation is working is essential. However, there should be no reason to suspect that a steel construction connected to a proper protection installation should not behave as if it were made of a noble metal. As the normal maximum cost of a protection installation is below 10 % of the cost of the foundation, such a protection installation will pay for itself many times over merely through the price of the steel saved.

For each building special investigations and designs have to be carried out to determine the right dimensions of the equipment. Normally special tests on the site have to be carried out after the piles have been driven and before the anodes are installed, in order to find the right current and distances between the anodes. It is our experience that the necessary current never increases beyond 30–40 mA per m^2 of steel surface in the corrosive ground. In most cases the necessary current will be considerably lower, even in cases where the corrosivity is so high that unprotected steel cannot be permitted. As the necessary voltage varies with the conductivity of the ground and the size and shape of the anodes, it is not possible to say anything general on this point, but in normal cases the voltages vary between 2–3 volt as a minimum and 20 volt as a maximum. Consequently, the maximum energy will be of the order 300 mW per m^2 of the steel surface, this current running constantly. If we, for illustration, think of a normal large office building in south-eastern Norway, the total area of piles will be of the order of some thousands m^2, and thus the total electricity will vary from some few hundreds to about one thousand watt. Very often the necessary effect will be considerably lower, and in any case the cost of electricity for the protection installation will be much lower than what is normally used for light in corridors, staircases and basements.

With cathodic protection we will rarely have a pure case of a construction which is separate from all other constructions and located in pure inorganic soil. In most cases there will be connection to other constructions which may undergo corrosion, or there may be electrical equipment in the vicinity with the associated possibility of stray current. In many cases sulphate-reducing bacteria may also be present. These bacteria, which may live without access of free oxygen, take energy from reduction of sulphate ions to sulphide ions by means of 8 electrons from the cathodic part of the steel construction; simultaneously 4 iron ions are liberated on the anodic part. Thus the biological electrochemical processes are not different in principle from the purely inorganic processes, and may be effectively stopped by cathodic protetion. However, it seems as if a somewhat lower potential is required to protect against bacterial corrosion than against pure inorganic corrosion. While it seems to be sufficient to bring the steel down to a potential of –850 mV against a copper/copper sulphate half cell in case of inorganic corrosion, it seems that this potential must be reduced to –950 mV in the case of bacterial corrosion.

In most densely populated areas as well as in the surroundings of industries using electricity, corrosion phenomena may occur as a result of stray currents. Such damage is commonly found in the vicinity of rails for street cars. Most street cars run on direct current, and usually the rails represent the negative terminal. From such street car rails one component of the current will pass through the ground to the rectifying station or power station, whereas another part will follow the rails. The component of the current which passes through the soil will on its way back to the rectifier frequently pass pipelines, piles or other good conductors. If the pipes or the piles pass through inhomogeneous soils with variable conductivity, the result is inevitably that one component of the current must leave the metal conductor in some places, and create an anode on these parts. This involves a corrosion process which will shorten the life of the construction.

It is not normally difficult to prove the existence of such stray currents, if the potential of the construction is measured against a standard cell, and if this potential is followed on a voltmeter for some time. In this way we may register on the voltmeter the passing of street cars and railways, or we may see when machines are working or shut down. It has to be kept in mind that many soils may act as imperfect rectifiers against alternating current, especially in cases where the current enters and leaves the soil through contacts of different sizes, or through contacts in soils of different conductivity. Thus most machines working on alternating current may create a certain current in the ground. Moreover, even pure alternating current may cause corrosion damage, although such stray currents may not be registered by a normal voltmeter. The alternating current, however, is easily registered on an oscillograph. If stray currents of some kind are registered in a construction, we have to assume that local or regional anodic corrosion at an increased rate will take place. Under such conditions an impressed direct current from protection equipment will be an effective help. The design of an equipment in such a case may be more difficult, and the necessary voltage may be higher than for normal corrosion. As a localised corrosion on pipes may take place far away from where the pipe line is crossed by rails, it is not possible to give a general statement as to how such a protection equipment should be arranged. In any case the cathodic protection involves a current through the soil, and in unfavourable circumstances this current in the ground may cause corrosion on other structures. It is therefore necessary to avoid mutual influence between such installations, and close co-operation between building, electricity, and telegraph authorities should be a rule. We need guidance on the design of all equipment which leads electricity down into the ground.

In harbours where some sheet piles and laid-up ships are protected, the current may cause corrosion on other ships which are not protected and which lie in such position that a certain component between the anode and the cathode passes the ship.

Similar cases may take place in soil. In Scandinavia we have relatively thick layers of soft clays of variable conductivity, and there is undoubtedly a great possibility for stray currents from all electric protectional installations. It is not uncommon for pipelines, cables etc. to be in contact with the reinforcement steel of a building, and this reinforcement steel in turn may have contact either with the anode or with the cathode. Thus under unfavourable conditions we may have a current running in one or the other direction through pipes or cables. The reinforcement of electric cables is normally not sufficiently well insulated from the soil, and pipes are normally not insulated at all. In cases where such conductors have a long horizontal extension, it is a great advantage if the pipe or the reinforcement of the cable could be broken by insulating flanges in some way or other before they enter buildings which are founded on piles fitted with galvanic protection. In the same way insulating flanges with nylon screws shoul be used where possible on pipes passing through soil where stray currents may exist, i.e. in the neighbourhood of street cars or railway lines, or other institutions using electricity, especially where these machines are grounded, and direct current is employed.

In cathodic protection in soil or sea water we have a gradual polarization of the protected structure. This polarization consists of a nearly instantaneous formation of a hydrogen film on the surface of the metal, and a slow precipitation of calcium and magnesium salts, especially carbonates. The *p*H of the ground surrounding the piles will increase slowly. With structures in soil where the flow of ground water is low, we have a nearly stagnant liquid phase, and an increase in *p*H will involve an effective corrosive protection, so that even in cases where the installation might fail we have, after some time, changed the medium from the *p*H range where corrosion is possible to a *p*H range where steel is either immune or passive. At the same time the steel will be more or less completely covered by a continuous layer of precipitated carbonates of calcium, iron and magnesium together with other salts of low solubility.

b. Protection by means of sacrificial anodes.

During the last decades magnesium and zinc have been used especially as material for sacrificial anodes. The first attempts to use zinc for proection of ship hulls were not especially successful. Later magnesium and magnesium alloys have been investigated as material for sacrificial anodes, and useful results have been obtained. In the later years zinc has again entered into the picture as a suitable metal. Pure magnesium has a driving potential versus polarized steel of the order of magnitude 840 mV, but due to anodic polarization which takes place during the corrosion of the magnesium the driving potential will be somwehat lower, normally of the order 700 mV. Only in indefinitely slow corrosion does the higher potential exist. However, even 700 mV is more than sufficiant to keep the steel in the protected range. Magnesium is a light metal, and the present industrial production makes it possible to use it with advantage in several cases. Magnesium has the following properties:

Atomic weight	24,3
Valency	2
Specific gravity	1,74
A · h/kg	c. 2 000

Pure magnesium and most magnesium alloys of low content of alloyed metals corrode rapidly in aqueous solutions, $Mg \rightarrow Mg^{++} + 2e^{-}$. The reaction which takes place in aqueous solutions normally follows the equation:

$$Mg + 2H^{+} \rightarrow Mg^{++} + H_2\uparrow$$

This reaction is irreversible and takes place at a less negative potential than theoretically calculated. For this reason the concentration of metal salts in the electrolyte is of little importance for the potential of the metal.

There are three electrochemical properties of magnesium which make it suitable for sacrificial anodes:

1. The driving potential versus protected steel is high.
2. The electrochemical equivalent weight is low.
3. The anodic polarization properties are good.

A piece of pure magnesium in an aqueous salt solution has a potential of – 1 700 mV against a copper/copper sulphate half cell. Supposing that magnesium is corroding according to the bivalent reaction mentioned above, we have a theoretical output of 1 A year for about 4 kg of magnesium. However, it seems that under certain circumstances we have a primary corrosion taking place by a monovalent reaction. Consequently the necessary amount of magnesium is doubled, i.e. about 8,5 kg/A year. In practice we rarely find more than 50 % effectivity with the use of magnesium for corrosion protection. This is, however, too expensive a way to produce the necessary protectional current. The fact that only bivalent salts are found among the corrosion products of magnesium does not exclude a primary monovalent corrosion. The presence of bivalent salts may be due to an immediate secondary oxidation without production of any protectional current. As the corrosion products of magnesium under normal conditions consist of easily soluable chlorides and sulphates, the anode does not undergo any marked polarization. In pure fresh water or electrolytes which do not contain chlorine or sulphate ions a precipitation of hydroxides or carbonates may occur. However, these precipitates do not cause any serious polarization, and even small amounts of sulphate or chloride ions in the medium are sufficient to cause an effective anodic depolarization. These ions may be added to the anode chamber by back-filling the anodes with a fill material containing gypsum.

Earlier experiments using magnesium for sacrificial anodes were not very successful. To-day, however, alloys containing 6 % of aluminium and 3 % zinc have proved very satisfactory. In commercial anodes the iron content is limited to max. 0,003 %, whereas manganese may be added to at least 0,15 %. Especially in case of sea water the content of magnanese has proved beneficial.

In the later years high purity magnesium anodes have been delivered and have proved to be satisfactory. The driving potential against polarized steel is up to 25 %

higher than with alloyed magnesium, and this may be advantageous under certain circumstances. The advantages of the new metals lie in the micro-structure and the methods of production are therefore of the greatest importance. Magnesium anodes are mostly used for ship production. In dry soil the precipitation of oxidation products around the anodes may be so large that it will increase the resistivity around the anodes, and the effectivity is consequently reduced because of the low current density.

Zinc is another metal which has found commercial use in ship protection. In Sweden, zinc protection of mast foundations has been employed (TRÄGÅRDH 1956). Zinc has a potential of – 1 150 mV versus a copper/copper sulphate standard cell, and consequently should have a driving potential of 0,3 volt against cathodic protected steel. It is a fairly cheap metal. Its most important constants are as follows:

Atomic weight	65,4
Valency	2
Specific gravity	7,1
A · h/kg	c. 825

The reason why zinc has not proved particularly effective for protection is the formation upon the metal of a continuous layer of corrosion products with high resistance. Much work has been done on the prevention of this anodic polarization, and various zinc alloys have been proposed for sacrificial anodes. These anodes have been reported to have a driving potential of – 200 to – 250 mV versus protected steel. Zinc corrodes according to a bivalent reaction, and the theoretical consumption of anodes is 10,4 kg per amp. year. This corresponds very well with results obtained in practice. 11,3 kg has been reported (MORGAN, J. H., 1959). The corrosion of zinc anodes is very even. Zinc anodes of extremely high purity will generally have a coarse-grained structure, and this may give rise to an extra loss of zinc because of the formation of insulating zinc oxide between the single grains. Zinc is mostly used under marine conditions. In soil, a backfill rich in gypsum around the zinc sacrificial anodes is recommended. It seems as if the presence of phosphates and salts having a high *p*H value, such as sodium carbonate etc., must be avoided. Because of the relatively low driving potential it is important that the backfill be compacted to high density, so that no unnecessary resistance is involved. It is also important that the anodes be kept moist; they may be placed below ground water level, or a hygroscopic moistening agent may be added.

As the necessary current to protect steel is fairly high, zinc anodes are rarely used when the resistance in the soil is above 500 ohm cm. However, zinc-covered steel, normally galvanized steel, may be effectively protected even in a soil of much higher resistance.

c. Anodes with impressed d. c.

When direct current is impressed from a rectifier, steel may be protected using a much lower number of anodes, as each of them may be used at higher current densities, and the driving potential may be much higher than is the case with the natural corrosion of sacrificial anodes. A voltage up to 20 volts has been used, although lower voltages are normally employed. With impressed d. c. the cathodic protectional current may be regulated through resistance or a transformer on the primary side of the rectifier. It is therefore much easier to apply the right amount of current, which is often difficult with sacrificial anodes.

The anodes which may be used with d. c. may be divided into three groups: the permanent, the semi-permanent, and the consumed anodes.

d. Permanent anodes.

The permanent anodes which were used were of graphite or carbon. Such anodes had far from ideal mechanical properties, being brittle and often porous. Thus it is not possible to apply high current densities without consumption occurring due to the development of gas in the outer layers of the anodes, which may give rise to such high gas pressures that the anodes disintegrate. Impregnation by resin, oil, or wax has mitigated this to a certain extent, but we still have to take a consumption of the anodes in account if the current density increases above 10 $A \cdot m^2$, but a current higher than 3 $A \cdot m^2$ is not recommended. In Norway, we are normally using rod-formed anodes of 3″ diameter and 60″ length with a plastic insulated cable. The point were the cable enters the anode is critical, and moisture must not be allowed to enter the anode, otherwise the contact may be destroyed. Often the transitional resistance from graphite to soil is high, and a backfill material of coke, or a mixture of coke, gypsum, and clay, has been used with advantage. However, in our saline clays it seems as though such backfill material is not necessary.

The construction of protection equipment depends upon the local conditions, especially the resistance of the soil. Normally we have found it disadvantageous to place the elctrode too near the steel construction which is to be protected. When the distance is too short, we have over-protection in the nearby steel, and an unnecessary use of current. With homogeneous conditions we have found that the ratio between the shortest and the longest distance between the anodes and the steel construction to be protected should not be less than 1:10, i.e. if a pipe extending 100 m on each side of the anode is to be protected, the anodes should be placed at least 10 m from the pipe. Fig. 32.

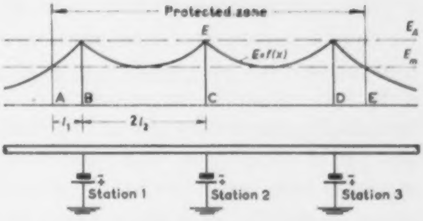


Fig. 32. Distribution of the protective potential along a section of "finite lengths." (After Pritula 1953.)

In water-front constructions where sheet pile quays are to be protected, such a distance for the anodes will often be difficult to arrange, particularly if the anodes are to be placed on the water side of the sheet pile, where dredging of the bottom must be expected. Under such conditions it may be desirable to place an insulating screen between the anode and the sheet pile wall, so that the effective distance between the anode and the nearest part of the sheet pile wall is increased. However, the anode may often with advantage be placed on the land side of the wall below ground water level, as the conductivity conditions in the soil make it possible to protect effectively even the water side of the wall in this way. In saline soils it is the transitional resistance that is the most important. At a distance of some few metres from the anodes the cross-section of the soil is so great that, for practical purposes, we may consider the resistance equal to zero.

Other permanent anodes have been constructed of platinum or platinated titanium. As far as we know, such anodes have not been used in soil. For ship protection, however, they have proved successful. It is necessary to keep the driving potential below a certain voltage, which may be of the order of 10 volt, otherwise the anodic passivation of the underlying titanium may be ineffective. As platinum is sensitive towards alternating current, it is essential to have a good rectifying equipment.

e. Semi-permanent anodes.

Ferrous silicon or iron of high silicon content has been used for semi-permanent anodes. Some anodic corrosion takes place. The consumption of anodes seems to vary in the various experiments, but with sufficiently low current densities, i.e. below 20 $A \cdot m^2$, less than 100 g anodic corrosion per Ampère-year has been observed. As the current density increases, there is a rapid increase in the anodic consumption. Thus, at 100 $A \cdot m^2$ a consumption of 1 kg per Ampère-year has been observed (APPLEGATE, L. M. 1960). The anodic attack takes place by localized pitting, and this uneven attack may bring the anodes to failure in a much shorter time than that calculated from the corrosional loss. We have no personal experience with such anodes in soil. Their mechanical properties do not seem to be much better than those of graphite. They can only be worked by grinding, and they are extremely brittle. Difficulties during transport are considerable, and the connection of anode cables is a difficulty.

Lead alloys may also be used, but we have no special experience of these.

f. Non-permanent anodes.

Anodes consisting of scrap iron, scrap steel, or aluminium have been use. Here we have a considerable consumption resulting from anodic corrosion. Theoretically, scrap iron anodes will be consumed at a rate of 9 kg per Ampère-year. With the low prices for scrap iron ruling at the present time such anodes may often prove economic, especially in case of quays. In a practical installation we may expect an output of 50–60 Ampère-year per ton of scrap iron. The anodes are strongly polarized, and the electrical resistance increases with use. They are thus not too effective in protecting piles in soil, but in sea water, especially when the water is moving, the corrosion products are removed, so that quays, laid-up ships etc. may be protected by means of scrap iron anodes. In case of aluminium we have a consumption of about 5 kg per Ampère-year. In salt water the corrosion products do not harm, in fresh water, however, the products will slowly increase the resistance,

g. Anodic protection.

Whereas the cathodic protection is based upon the lowering of the potential of a metal construction through bringing it below the "dangerous triangle" in the Pourbaix diagram, the anodic protection is based upon an increase of the potential, so that the metal is covered by a protective film of oxides or chemisorbed oxygen. It is, however, difficult to protect steel in this way. If the passivation is incomplete, an anodic protection may cause more damage than if it had not been installed. In other cases, where the liquid phase has a high *p*H value and the mobility is high, such methods have been considered. In this connection we do not recommend anodic protection.

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